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Applicability of Land Treatment of Wastewater in the Great Lakes Area Basin: Effectiveness of Sandy Soils at Muskegon County, Michigan, for Renovating Wastewater

Michigan State Univ., East Lansing

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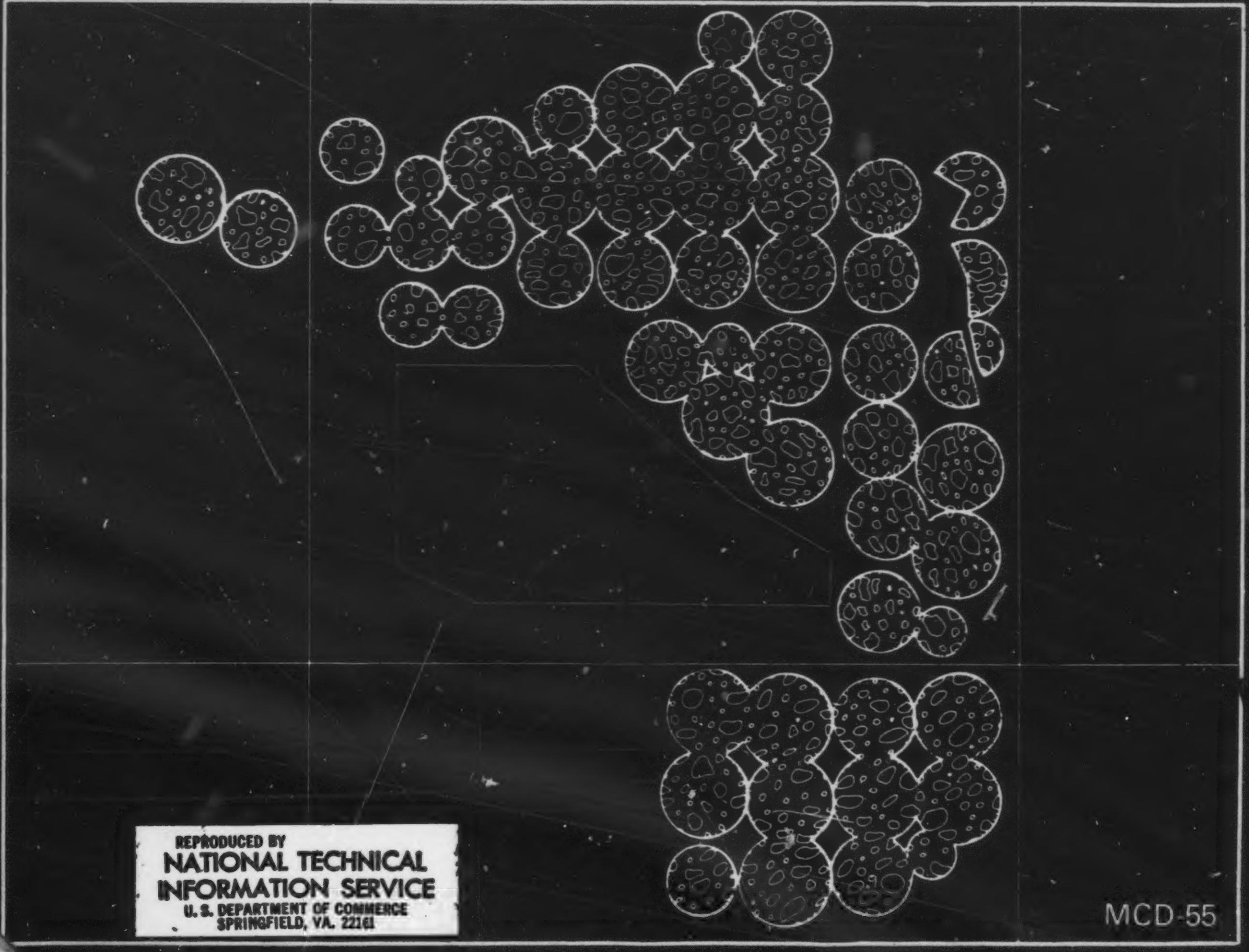

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Preface

The U. S. Environmental Protection Agency was created because of increasing public and governmental concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment.

The Great Lakes National Program Office (GLNPO) of the U.S. EPA was established in Region V, Chicago, to provide specific focus on the water quality concerns of the Great Lakes. The Section 108(a) Demonstration Grant Program of the Clean Water Act (PL92-500) is specific to the Great Lakes drainage basin and thus is administered by the Great Lakes National Program Office.

Land disposal of wastewater in the Great Lakes area is one alternative for treatment that can provide tertiary quality effluent when properly managed. This report evaluates the effectiveness of sandy soils at Muskegon County, Michigan, for renovating wastewater.

We hope the information and data contained herein will help planners and managers of pollution control agencies to make better decisions in carrying forward their pollution control responsibilities.

Edith J. Tebo, Ph.D.
Director
Great Lakes National Program Office

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The Muskegon County, Michigan Wastewater Management System

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16. ABSTRACT

The Muskegon County Wastewater Management System is a lagoon impoundment, spray irrigation facility which treats about 102,000 cubic meters of wastewater per day and irrigates 2,160 hectares of corn land. About 60% of the flow is industrial. Data was collected over a three year period to determine the changes from background conditions of the native infertile sandy soil as wastewater was irrigated and crops grown. Data analyzed include major crop nutrient elements and heavy metals, the soil physical properties and electron capturing organic chemical species.

The knowledge gained was used to estimate the useful life of the system for removing critical contaminants such as phosphorus and metals relative to the amounts of contaminants and wastewater applied. With proper management phosphorus can be removed by soils and crops for at least fifty years. It is not expected that soil physical properties will offer any major problem hydraulicly for the rate and type of wastewater being applied. Removals of trace organics from the wastewater occurred in storage lagoons and as the water passed through the soil mantle, however, with partial pass through of certain organics occurring when the wastewater application rate was excessive. This system apparently became more effective with time in removing many of these trace organic chemicals.

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APPLICABILITY OF LAND TREATMENT OF WASTEWATER IN THE GREAT LAKES AREA BASIN:

EFFECTIVENESS OF SANDY SOILS AT MUSKEGON COUNTY, MICHIGAN, FOR RENOVATING WASTEWATER

by

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EPA REVIEW NOTICE

This report has been reviewed by the Office of Research and Development and the Great Lakes National Program Office of Region V, U.S. EPA, Chicago, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Great Lakes are the world's largest fresh water resource. It is shared by the United States and Canada. In the U.S., this lake system serves important water needs of people and industries in eight states, six of which comprise the area served by EPA Region V. The usefulness of the lakes, for many purposes, has been impaired by past misuses of the lakes themselves and of land resources in contributing drainage basins. Management of the Great Lakes Area Basin to halt or reverse the degradation of vital water resources is of great importance to both countries. Lake Michigan presents special concerns because of its headwater relationship to the lower Great Lakes and because of the intensity and variety of human activity that impacts upon it. Responsibilities for developing and enforcing ameliorative management in the Lake Michigan basin rest with the U.S. and the four states that share the shoreline of the lake.

Land application of wastewater is one of the management options for upgrading water after use. From historical precedent and for many theoretical reasons, land application has the potential for effecting full renovation of wastewater before release into the environment. Whether this potential is realized will depend on many factors of soil, climate and management which must be understood for each situation. Performance must be assessed ultimately in terms of impact on contiguous aquatic systems. The acquisition of background and early operational data for a large land application system in Muskegon County, Michigan, has been the objective of an intensive three-year study conducted for EPA Region V by the Michigan Water Resources Commission, with subcontracts to Michigan State University and the University of Michigan. The three reports covering this work carry the general title, "Applicability of Land Treatment of Wastewater in the Great Lakes Area Basin," with respective subtitles:

> The Muskegon County System--An Overview, Monitoring Considerations and Impacts on Receiving Waters.
>
> Effectiveness of Sandy Soils at Muskegon County, Michigan, for Renovating Wastewater.
>
> Impact of Wastewater Diversion, Spray Irrigation on Water Quality in Muskegon County, Michigan, Lakes.

In these volumes, data collected from 1972 through 1975 are evaluated in relation to the applicability of land treatment for renovating municipal and industrial wastewaters in Muskegon County. Short-term and long-term projections are made regarding management practices that can influence the renovative effectiveness of soils and crops. Observed and projected effects of wastewater diversion and treatment on water quality and ecosystem responses in lakes and streams that drain into Lake Michigan are described.

ABSTRACT

A key concept in design of the Muskegon Wastewater Management System is the use of soils and crops as a "living filter." Management to achieve a desired degree of renovation at acceptable cost requires a knowledge of changes that occur in water as it passes through the system, as well as a knowledge of changes in soil that can be projected to estimate useful life of the system.

Four major soil types (Rubicon sand, AuGres sand, Roscommon sand and Granby loamy sand) comprise a majority of the land area on the Muskegon wastewater management site. Analysis of soil profile samples representing each of the four major soil types were conducted to determine the level of Kjeldahl N, NO_3, NH_4, Ca, Mg, Na, K, P, Fe, Zn, Mn, Cu, Hg, Pb, total C and pH prior to application of wastewater and after application of wastewater during 1974 and 1975. Summaries of data are given in this report. Some nitrate moved through the soil profiles, apparently more the result of initiating the farming operation than from applying wastewater. Phosphorus was being adsorbed by the Rubicon sands and Roscommon sands. The AuGres sands did not appear to be adsorbing P, and insufficient wastewater had been applied to the Granby loamy sands to make a valid inference. Soils which had received more than 300 cm of wastewater had reached an equilibrium with respect to Na, Ca and Mg which allowed most of the Na applied to pass through the soil profile. Soil pH was increasing and should approach the pH of the wastewater in a few years. There was no apparent accumulation of heavy metals in the soils due to a very low input of metals.

Soil physical properties were evaluated by measurement of infiltration rate, hydraulic conductivity and bulk density. The majority of these very sandy soils will conduct water so fast that infiltration and hydraulic conductivity should not be a problem. However, a small percentage of the soils mapped as Saugatuck or AuGres have been observed to have very slow hydraulic conductivities.

Electron-capturing organic chemical species were monitored in soils and waters, using multi-column gas-liquid chromatography and thin layer. Patterns of encounter with 26 pesticide parameters in incoming wastewater are evidence that chemicals from non-point sources can enter through feedwaters taken from lakes and streams by industries that discharge into the system. By inference, chemicals that originate in extramural point-source discharges can enter also. The potential problem from industrial trace organics originating within the service area was addressed only superficially by analytical protocol employed in this study. Evidence was obtained for chronic entry, at substantial concentrations, of diethylhexylphthalate and three unreferenced electron-capturing species. Removals of trace organics from wastewater occurred in storage lagoons and during passage through the soil mantle. Chromatographic peaks observed in incoming wastewater and peaks for pesticides used on site were found in extracts of soils sampled after the system was placed in operation. Intercepted chemicals were found mainly in surface and shallow subsoil layers. Organic chemicals detected in drainage at outfalls were associated with heavy rains and with seasonally heavy applications of wastewater on restricted soil areas. Frequency and concentration at outfalls for chronically input chemicals declined from 1974 to 1975. This suggests developmental changes in lagoons and soils leading to increased effectiveness in removal of these chemicals from wastewaters passing through the system.

This report was submitted in fulfillment of a subcontract by Michigan State University to Michigan Water Resources Commission as part of their Grant No. G005104 under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period of April 1, 1972 to December 31, 1975, and work was completed as of June 30, 1976.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

$\bar{X}$ -- mean
SD -- standard deviation
ppm -- parts per million
ppb -- parts per billion
me -- milliequivalent
ml -- milliliter
cm -- centimeter
g -- gram
kg/ha -- kilogram/hectare
ng/g -- nanograms/gram (ppb)
ng/l -- nanograms/liter (parts per trillion)
GLC -- gas-liquid chromatography
TLC -- thin layer chromatography
GC-MS -- mass spectrographic analysis of chemical species isolated by preparative gas chromatography
ECD -- electron capture detector

SYMBOLS

N -- nitrogen
P -- phosphorus
K -- potassium
Ca -- calcium
Mg -- magnesium
Na -- sodium
Zn -- zinc
Cu -- copper
Mn -- manganese
Fe -- iron
Pb -- lead
Hg -- mercury
Cr -- chromium
C -- carbon
NH_4^+ -- ammonium ion
NO_3^- -- nitrate ion

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SECTION I

SUMMARY AND CONCLUSIONS

GENERAL

Baseline data has been established for the major soil types at the Muskegon land treatment system (Rubicon sand, Roscommon sand, AuGres sand, and Granby loamy sand) for physical properties, chemical analysis, heavy metals, pesticides, and certain industrial organics, microorganisms, and arthropods. Establishment of the baseline levels and the soil variability within the soil irrigation site allows for evaluation of the effectiveness of the land treatment process in renovating wastewater. Comparisons between baseline data and soil analysis after one or two years of application of wastewater will allow for predictions of the effectiveness of the system and possible management changes that must be made to improve the effectiveness of the operation. The soils were initially free of contamination from heavy metals. Very low levels of dieldrin and DDT species were indicated in most surface soils and many subsoils, using chromatographic methods and electron capture for detection.

CHEMICAL ANALYSIS

Both total and "available" nutrient analyses were determined for P, K, Ca, Mg, and Na on profile samples from each of the major soil types. Profile samples were collected twice yearly from 15 cm (6 inch) layers to depths of 305 cm (10 feet). Total C and N, distillable NH_3, soluble NO_3, and pH were also determined. From the data the following conclusions were drawn:

1. Available or extractable nutrients are much more sensitive to changes produced by wastewater application for P, K, Ca, Mg, and Na than is total analysis. Changes in the available fraction were detected after as little as 20 cm (8 inches) of wastewater application; whereas, few differences were noted in total analysis after application of more than 380 cm (150 inches) of wastewater.

2. The NO_3^- content of Rubicon, Roscommon, and AuGres sands is low. Furthermore, irrigation with the rather low N containing wastewater does not supply adequate N for maximum growth of corn during the period of peak demand (i.e., during the months of July and August), but during the remainder of the year some N as NO_3 is expected to be lost through the soil into the drainage water because it is present in excess of crop needs. In general, this quantity of N moving in the soil profiles was under 5 ppm N as NO_3, but occasional samples were much higher. The NO_3 tended to move in bands in the soil profiles. High values for NO_3 were more commonly found in the Granby soils and appeared to

originate from the oxidation of native organic matter in the surface layers and not from wastewater application.

3. Phosphorus was effectively removed from the wastewater applied to Rubicon sand by adsorption in the surface layers. The effective life of the Rubicon sand for removal of P by this mechanism should be more than 50 years at the present level of P input (less than 3 ppm P), average applications of 150 cm water per year, and with yields from 80 to 100 bushels of corn per acre. Initial data did not show a gain of P in the AuGres and Granby soils. This may be partially attributed to lower application rates, particularly for the Granby soils, but adsorption isotherms also indicated that these soils had lower adsorption capacities and that the AuGres soils may not bind P as tightly as the other soil series.

4. Uneven distribution of wastewater on the soil may adversely affect the life of the system. One site appeared to have received far less water in the sampling area than was reported which suggests heavier application in other parts of the circle. This can lead to P leaking at an earlier than predicted time.

5. Two years of application of wastewater was adequate to allow for passage of Na throughout the profile. A land treatment system is not effective in removing cations (Na, Ca, Mg and K), but rather the process that functions is one of cation exchange whereby adsorption of one base will result in release of another. Some adsorption of Na does occur in the soils with release of Ca, but an equilibrium is soon reached after which the water passing through the soil will be very similar in bases to the wastewater being applied. Our data would suggest that on all sites where greater than 305 cm (120 inches) of wastewater have been applied, the Na content of the tile drainage water should be the same as the water being applied. Where discharge water levels of Na are lower than in the wastewater, dilution by other drainage water has apparently occurred. The level of exchangeable Na at this equilibrium is not expected to cause appreciable change in the physical properties of these very sandy soils. High levels of Na in soils may lead to dispersion of clay and organic matter and reduced infiltration of water. Rubicon, Roscommon and AuGres sands are so low in clay and organic matter content that they are unlikely to be affected by the levels of Na in the wastewater. If any changes do occur, they should be expected on the Granby soil which is considerably higher in organic matter. Insufficient water has been applied to the Granby soils at this time to ascertain if there will be any dispersion effects in the soil resulting in decreased ability of the soil to accept water.

6. Potassium is moving through the soils and leaching into the discharge waters. This occurs because the concentration of K is much lower in the water being applied than is the concentration of Ca and Mg and does not compete favorably with Ca and Mg for exchange sites. In addition to concentration, a major factor is that the monovalent K ion is not bonded as strongly to the exchange complex as are the divalent Ca and Mg ions.

7. Total C content of Rubicon, AuGres and Roscommon soils is very low. Hence, these soils are very effective in eliminating BOD from the applied

wastewater. An increase in organic matter (C) would likely increase the agricultural productivity of these soils. This could be accomplished through application of sludge. Since the Granby soils are already high in total C in the surface layers, low in P adsorption capacity, and release N by decomposition of organic matter, an application of sludge would not be desirable, but if well drained, the Granby soils will function well in reducing BOD from wastewaters.

8. Soil pH is increasing rapidly with the application of wastewater and should stabilize within the next two years to a level near that of the incoming wastewater. The soil adsorbs Ca, Mg and Na from the wastewater and the H replaced is neutralized by the basic water. This pH is slightly higher than is desirable for agronomic purposes but should pose little problem.

9. Low soil pH's resulted from draining and aerating the Granby soils prior to application of wastewater. This is usually a result of oxidation of S that has accumulated in the subsoils. As a result, Fe was mobilized and moved into the drainage water. These soil pH values are increasing due to movement of bases down in the profile after application of wastewater and to soil chemical reactions. Iron in the soil should soon stabilize as the pH increases above 4 to 5.

PHYSICAL MEASUREMENTS

Initial clearing and beginning farming operation of these soils has left them so variable in the surface layers that meaningful physical measurements are difficult, and it is impossible to establish trends from the short period of time that wastewater has been applied. But the following conclusions may be drawn:

1. Infiltration rates are so high on all major soil types that it is difficult to imagine that this will ever become a limiting factor. But some microareas of Saugatuck sand may have limited infiltration.

2. All aeration measurements have shown a high degree of aeration except where there are definite drainage malfunctions. Therefore, once drainage is improved, aeration should be no problem.

HEAVY METALS

Selected total and chelate extractable micronutrient and heavy metal analyses were conducted on soil profile samples. The elements determined were Fe, Mn, Zn, Cu, Pb, and Hg on samples taken at 15 cm (6 inch) intervals down to a depth of 305 cm (120 inches) in Rubicon sand, Roscommon sand, AuGres sand, and Granby loamy sand which are the main soil types on the wastewater treatment site. From the data, the following conclusions were drawn:

1. Total analyses indicate that none of the soil metals were increased significantly by the addition of wastewater. Lead and Hg, which are of particular concern, are still at levels below the detection limits of the methods used. Zinc which may have been added in amounts up to 0.2 ppm Zn in the wastewater, did not show any total accumulation, even though 7.8 kg/ha of Zn

per acre could have been added at sites receiving more than 380 cm (150 inches) of wastewater. Crop removal would account for less than 1 kg/ha of Zn. Therefore, Zn should be detected in the surface samples in the next few years if the level in the irrigation water is greater than 0.1 ppm Zn.

2. Total Fe values fluctuated considerably throughout the soil profile, but there was no obvious change in Fe content with profile depth. Total Cu and Zn, and to a lesser extent Mn, were localized in the top 15 cm (6 inches) to 30 cm (12 inches) of soil. The initial concentrations appeared to be associated with the organic matter in the surface layer of the soil. After plowing, the total Cu, Zn, and Mn were distributed to the depth of the plow layer, but they did not move by leaching below that point over the duration of the study. The total quantity of heavy metals applied in wastewater (380 cm) was very small compared to the total initially in the soil (less than 0.1 percent in all cases). The localization of total Cu, Zn, and Mn in the surface layers was most pronounced in the Rubicon sand. By contrast, the total Mn was relatively evenly distributed throughout the soil profile of the Granby soil. The other soils fell between these extremes. The Mn in the lower profile of the Granby sand can be explained by the relatively flooded (reducing) conditions in the soil prior to drainage. The flooded conditions favored the formation of the relatively soluble manganous ion (Mn^{+2}) which could move through the soil profile. In contrast, conditions in the well-aerated Rubicon sand favored the formation of the manganic ion (Mn^{+4}) which forms relatively insoluble oxides that cannot move in the soil profile. Also, much of the Mn appeared to be associated with and bound to soil organic matter, and Rubicon sand contained little organic matter below the soil surface. Since solubility of Cu and Zn are not significantly influenced by soil oxidation-reduction status, there were no pronounced changes in their soil profile distributions as the result of aeration status.

3. Chelate extractable soil micronutrients were determined to estimate the magnitude of an "available" fraction which is potentially available for plant uptake and to movement through the soil profile with irrigation water. The relative degree of extractability closely paralleled the total amount of micronutrient in the soil profile. The relative magnitude of extractability was as follows: Fe>Mn>Zn>Cu. Iron and Mn were the micronutrients most influenced during the time frame of the investigation. The changes which were observed were due to changing the oxidation status of the soil with soil water drainage and to disturbing the surface soil organic matter layer with the beginning of cultivation practices. Generally, the amount of extractable Fe and Mn was high in the surface layers of the soil initially and decreased as the organic fraction was broken up with cultivation practices. Extractable Fe in the surface layers decreased from a range of 50 to 200+ ppm Fe initially to 10 to 40 ppm Fe by the seventh sampling. Initially there were some relatively high amounts of extractable Fe (as much as 40 ppm Fe) in the lower levels of the soil profiles which had been flooded. However, as these soils were drained, the extractable Fe decreased to a background level below 10 ppm Fe due to leaching of soluble Fe and formation of ferric hydroxide in the well-aerated conditions.

Extractable Mn initially ranged from 1 to 40 ppm Mn in the surface layers. The extractable Mn levels below the surface layers dropped to about 1 ppm Mn and continued to decrease with time. Most of the extractable fraction was associated with the organic matter in the soil, and as the soil became well aerated, less Mn was extractable due to the formation of more insoluble manganese oxides.

Extractable Cu and Zn were less influenced by effects of management changes on the soil.

TRACE ORGANICS

Local and regional hydrologic systems were described in some detail, with a view to identifying probable sources and modes of entry for trace organics into wastewater collection systems at Muskegon and Whitehall. Electron-capturing species were monitored in monthly composites of incoming wastewater and outfall drainage over a two-year period. The same analyses were performed on extracts of soils sampled biennially, twice before and three times after wastewater irrigation was initiated at the treatment sites. Implications and limitations of the data are summarized here:

1. Patterns of encounter with 26 pesticide parameters provide evidence that chemicals from non-point sources can enter these systems through connected discharges from industries that take their feedwaters from Muskegon Lake, Mona Lake, White Lake or tributary streams. By inference, chemicals originating at extramural point-sources can be expected also.

2. A wide range of industrial chemicals which have become the focus of concern in these systems was not addressed by analytical methods used in this study. Credible evidence for chronic entry of DEHP was obtained. Peaks for several unreferenced electron-capturing species were present frequently in incoming wastewater but were not identified.

3. In background soil samples, dieldrin and DDT species were indicated at the very low concentrations that might be expected from global circulation, with evidence at one sampling station for locally higher residues from earlier use.

4. Chromatographic peaks observed in incoming wastewaters and peaks for pesticides used on site were found in extracts of soils after the systems were placed in operation in 1974. Both referenced and unreferenced species were found mainly in surface (0-15 cm) and shallow subsurface layers (46-61 cm). Encounters at 91-107 cm were infrequent or at levels approaching the limit for quantitation.

5. Outfalls were monitored only at the Muskegon site. Detectable amounts observed for a number of chemicals were associated with heavy rains or with seasonally expedient modes of operation that resulted in unusually heavy applications of wastewater on limited soil areas.

6. Data for successive flow points at Muskegon indicate that removals of trace organics occurred both in storage lagoons and during passage through the soil mantle. Chemicals intercepted most effectively were those that are strongly adsorbed by soils or sediments and those that are readily metabo-

lized. Chemicals responsible for unreferenced GLC/ECD peaks appeared to be more recalcitrant or more mobile in soils than the referenced species.

7. Chemicals observed frequently in incoming wastewater (lindane, heptachlor, related species, DEHP) declined in frequency and concentration at outfalls from 1974 to 1975. This is hopeful evidence that the efficiency of the system in removing exotic chemicals may improve over time. Beneficial developmental changes may include the induction of adaptive enzymes in lagoons and soils, increasing volume and adsorptive surface of sediments in lagoons, and increased annual return of crop residues and exudates to support cometabolism of recalcitrant compounds in soils and residual increases in adsorptive soil organic matter.

MICROBIAL STUDIES

Limited microbial studies were made on three soil types representing the extremes in the Muskegon land treatment site before and after wastewater application. The populations analyzed for were nitrifiers, denitrifiers, aerobes, and anaerobes. The following conclusions were drawn:

1. There was initially a very low number of nitrifiers on the Rubicon and AuGres sands probably due to the very low soil pH. This also related to higher ammonium values on these soils. As the pH increased with wastewater application, the numbers of nitrifiers increased and ammonium disappeared. The Granby initially had high soil pH's and a high nitrifier population.

2. The denitrifier population relative to the total aerobes and anaerobes was quite low in all soils, but there was a slight increase with irrigation, particularly in the Rubicon soil.

3. Irrigation with wastewater had no detrimental effect on the soil microbial community.

SOIL ARTHROPOD STUDY

Samples of soil arthropods were obtained and studied from each of the four major soil types. The soil animals were extracted and sorted into major groups. The soil faunal categories found to occur in the study area were: Diptera, Diptera larvae, Coleoptera larvae, Hemiptera, Thysanoptera, Enchytraeidae, Nematoda, Oribatid mites, predatory mites, and Collembola. The major conclusion is that the site was and is very poor in both number of species and in number of individuals. If the soil organic fraction increased through application of sludge, the arthropod population would be expected to increase.

SECTION II

RECOMMENDATIONS

GENERAL

Soil monitoring information indicates that the Muskegon County land treatment site is generally operating in a satisfactory manner. The initial years' study indicates that certain areas should be monitored closely in the next few months but that other areas are changing slowly and that a number of years should elapse before reexamination of the latter areas. The following specific recommendations are divided into two general areas--management and research needs:

Management

1. The present balance between Na, Ca, and Mg in wastewater being applied to the various coarse soils at Muskegon is satisfactory for crop growth and soil structure, but the level of Na in this wastewater should not exceed 300 ppm.

2. Differential water applications should be made, with Granby soils receiving substantially less water than Rubicon or Roscommon soils, because the Granby soil has a lower P adsorption capacity, greater potential mineralization of native N, and possible problems with dispersion of organic matter if Na content becomes too high.

3. Non-uniform application of wastewater should be avoided. This practice may materially shorten the period of time that the soil is able to remove P from the wastewater. Adsorption and degradation of organic chemicals requires a period of time, and heavy application of wastewater may displace the organic chemicals before sufficient reaction time has occurred.

4. From a crop management viewpoint, available Mn and Zn both appear to be at a low level where plant deficiencies could be a problem. Sufficient Zn to prevent deficiencies may be added in the wastewater, but decreasing organic matter in the soils and increasing soil pH as a result of added wastewater may decrease the availability of Mn and Zn to plants. Soil and plant Mn and Zn levels should be monitored regularly to detect these possible deficiencies.

Research Needs

1. A detailed study should be made of N stripping in the field by agronomic crops to determine if both the period of effective NO_3 uptake by crops can be extended and if the level of NO_3 leaching through to groundwater can be

reduced. Initial data indicates that NO_3 is leaching during periods when the corn is not actively growing.

2. Phosphorus adsorption in the AuGres soils should be examined in detail because it does not appear to retain P.

3. Soil physical measurements should be made again after approximately five years of wastewater application to determine if long-term application will affect the physical properties of very sandy soils.

4. Areas of Saugutuck and a few areas of AuGres sands that are showing an inability to remove water through the installed drainage should be studied to suggest a management practice or improved drainage system that would function in these areas.

5. A close study of available heavy metals should be made in the next year. The quantity of Zn, for example, that was supposed to have been added in the wastewater should have been detectable in the soil but it was not found during the first year after wastewater was applied.

6. The monitoring of pesticides in soils at special study sites and of waters at various stages of treatment should continue to confirm developmental trends observed to date. Additional flow points should be sampled to increase the probability of detecting chemicals which enter sporadically.

7. Routine monitoring for critical trace organics in waters at key flow points within the collection and treatment systems is essential for rational management. This can best be done by personnel and facilities at the Muskegon site. Timely notification of anticipated critical discharges from connected industries will be essential.

8. An ordering of priorities among critical compounds considered for monitoring is essential to allow for development of analytical capabilities and methods appropriate for different classes of compounds and realistic in relation to available facilities, personnel and funds. Methods for a given chemical or group of chemicals should be evaluated and quality control parameters established before routine monitoring is undertaken. Chromatographic entities, when first encountered, should be identified by definitive methods.

9. Supporting research is needed to identify mechanisms affecting the fate of trace organics in pretreatment basins, storage lagoons and soil. There should be continuing concern for the possibility that specific toxicants might be transferred from wastewaters or sludges into animal feeds and human food channels.

10. Computerization will be required to accumulate, retrieve and manipulate the many kinds of information, from many sources, that are relevant to the management and regulation of these systems. Modeling studies should continue to this end.

SECTION III

INTRODUCTION

The methods of treating waste in the past have satisfactorily reduced BOD but have not removed nutrients. Discharge of effluents after primary and/or secondary treatment have often led to deterioration of rivers and lakes due to inputs of nutrients as well as organic matter. Federal and state regulations now require that wastewaters be minimally polluting when they are discharged into our waterways. Land treatment of wastewater is one alternative in removing polluting materials. This method may be effective in the treatment process, and it is also cost-effective in many cases; but equally important, it offers a method of treatment that recycles a portion of the nutrients directly back into the food chain, thereby offering conservation of nutrients.

Soil types are of prime importance in considering various land treatment alternatives. Fine-textured soils offer considerable advantage in that they are able to adsorb high quantities of P and other materials, but they have a major disadvantage in that they are unable to receive high rates of water. Oftentimes an application of just 2.5 cm of wastewater per week (1 inch), in addition to the normal rainfall, may lead to reduced aeration and poor yields. They would also require a considerable length of time after no water is applied before they could be farmed.

On the other end of the spectrum are the very sandy soils whose infiltration rate and hydraulic conductivity are very high. These soils can hydraulically receive considerable quantities of wastewater without aeration problems, but may not adequately remove P and other nutrients because of their low adsorption capacity, particularly at high rates of wastewater application. Drainage classification is another very important factor that must be considered in selection of soil types for land disposal. Since wastewater must move through the soil for treatment, it is imperative that the drainage of the soil either be good naturally or be developed into a good drainage system by the installation of tile drainage lines.

Some soils are poorly drained because of a very slowly permeable clay layer somewhere in the subsoil. Installation of tile lines above this layer may easily remove the excess water if the hydraulic conductivity of the upper profile is adequate.

Land treatment of wastewater is different from other more conventional methods. The performance of a land treatment system may be much better for its first few years of operation than thereafter because of the many sorptive and exchange reactions occurring in the soil which act as a buffer against rapid change. Thus a system may appear satisfactory during the first few years of operation but then suddenly begin to leak nutrients to the drainage water. Early detection of the changes that occur in the soil after application of effluent, therefore, becomes of major importance in estimating the life of the system and in showing operational changes that must be made to prolong the life or to produce a higher quality of effluent.

At the present time the Muskegon project is the largest land treatment system in the United States. It also has some unique features that make it different from most other land treatment systems. The site has very sandy, level soils, approximately two-thirds of which are, or were in their natural state, poorly drained due to the presence of a clay layer in the subsoils. This clay layer varies in depth but, before drainage, effectively kept a high water table under a large acreage on the treatment site. These soils have a very high hydraulic conductivity so that they remove water easily where a satisfactory tile drainage system has been installed. This site was marginal from an agricultural viewpoint without the installation of a drainage system and the application of water and nutrients during the growing season. The installation of drainage and irrigation systems necessary for treatment of wastewater is converting this marginal land into productive agricultural land. Because of the necessity of increasing world food production, simultaneous renovation of wastewater and its use to produce food is an important feature of the Muskegon system.

The wastewater being applied to the land at Muskegon is lower than average in nutrient content due to dilution by industrial wastewater from the S. D. Warren Paper Company. Consequently, the N and P contents of the wastewater after aeration and lagoon storage are about half that of an average effluent. This has two important consequences: 1) the requirement for P removal will not be as high, and the low P adsorption capacity of the sandy soils at Muskegon is of less importance than it might be for other wastewaters, and 2) the N content of the wastewater is sufficiently low that an agronomic crop may be expected to be N deficient during much of the growing season; thus, management of this system must consider the application of N during the critical periods of growth.

To construct and make the Muskegon land treatment system fully operational, land was cleared where the native vegetation was shrubs and trees, drainage systems installed (usually tile) where necessary, and the land surface was tilled until it became suitable for growth of crops capable of removing nutrients from the wastewater.

During these clearing and construction phases, many changes may occur in the soil properties, both chemical and physical. Drainage and cultivation are expected to produce better aeration of the soil and result in decomposition of soil organic matter. As a result, total soil C may decrease. With the decomposition of organic matter also comes the release of N through ammonification and then oxidation of NH_4 to NO_3. The results may be an increase in NO_3 in the drainage waters.

The relative distribution of bases (Ca, Mg, and Na) in soil at various depths to the groundwater table is not expected to change greatly with the initial preparation of the site, but they will change rapidly with the addition of wastewater. Soil pH, a related chemical property, is expected to increase with application of wastewater due to the replacement of H^+ with basic cations.

Heavy metals may be associated with the organic matter in the soil. Consequently, oxidation of the organic matter may cause a redistribution of the heavy metals. Also, pH and oxidation changes within the soil profile would be expected to exert major changes on the solubility of heavy metals and the distribution between organic and precipitated phases.

A major goal of this study was to determine soil chemical and physical properties prior to and during preparation of the site; and, once having established this baseline data, being able to clearly delineate changes brought about by the application of wastewater to the land as separate from changes brought about during preparation of the site.

The objectives of the study were to:

1. Determine the quantity of N and C adsorbed or stabilized by other means in the various soils.

2. Determine the quantity of P, K, Ca, Mg, Zn, Cu, Mn, Fe, Pb, Hg, Cr, and Na adsorbed by soils.

3. Determine the changes in physical properties of the major soil series receiving effluent.

4. Monitor electron-capturing organic species in soils, in incoming wastewaters, and in drainage at outfalls.

5. Prepare soil samples for preservation as background and base level samples for future measurements of other ions of interest.

To accomplish these objectives, a major portion of this study was devoted to establishing the background for the site and the variability in the soils that could be expected.

Detailed data have been reported in many quarterly reports over the past three years. In the case of mineral analyses and physical measurements, only summary data will be included in this final report. Table 1 has been prepared to show the location of previously reported data. All data collected to date for pesticides and other trace organics are reported here and should supersede previously reported data.

A knowledge of the water applied to each of the individual circles or sites is important in interpretation of the data; consequently, a table has been included from data furnished by the County of Muskegon indicating the quantity of water that was applied by sampling periods (Table 2). Total ion concentrations, together with sampling dates, are included in Table 3. Specific site locations are given in Figure 1.

Table 1. LIST OF CHEMICAL ANALYSES DATA REPORTED DURING PROJECT PERIOD.

Parameter	Table No.	Sampling Period	Sites Reported	Report Date
Extractable NH_4, P, K, Ca Mg, and Na	1	1	1-8, 10-12, 14-26 28-32	April 1973
Soluble NO_3 pH	1	1	9, 13, 27, 33-37	April 1975
	1	2	1-37	April 1974
	1	3	1-37	June 1974
	1	4	1-37	April 1975
	1	5	1-6, 10-12, 14-15, 18-19, 21-23	Sept. 1975
	1	6	1-37	April 1976
	1	7	1-37	April 1976
Total N, C, P, K, Ca, Mg, and Na	2	1	1-5, 8, 10-21, 23-31	Oct. 1973
			6, 7, 9, 22, 32-37	April 1975
	2	2	1-37	April 1975
	2	3	1-37	April 1975
	2	4, 5, 6, 7	1-37	April 1976
Extractable Fe, Mn, Zn, Cu, Pb, and Hg	3	1	1-37	April 1975
Total Fe, Mn, Zn, Cu, Pb, and Hg	3	2	1-37	April 1975
	3	3	1-37	April 1975
	3	4, 5, 6, 7	1-37	April 1976

Table 2. WASTEWATER APPLICATION TO SAMPLING SITES*.

Site No	Circle No	Soil Type	May 74 to Dec 74	Jan 75 to Jun 1,'75	Jun 2 to Sep 1,'75	Sep 1 to Dec 31,'75	Totals
			cm				
01	5	Rubicon Sand	216	57	104	74	451
02	8	Rubicon Sand	214	57	94	58	423
10	2	Rubicon Sand	212	67	74	67	420
11	1	Rubicon Sand	149	68	60	53	330
12	22	Rubicon Sand	196	28	87	68	379
14	11	Rubicon Sand	200	12	102	44	358
18	3	Rubicon Sand	196	0	102	74	372
19	7	Rubicon Sand	232	57	112	61	462
09	42	Roscommon Sand	55	0	115	3	173
13	31	Roscommon Sand	53	7	86	18	164
15	12	Roscommon Sand	193	23	80	53	349
16	41	Roscommon Sand	75	14	46	7	142
17	42	Roscommon Sand	55	0	115	3	173
20	40	Roscommon Sand	48	7	31	11	97
21	19	Roscommon Sand	139	0	71	58	268
23	27	Roscommon Sand	172	19	92	43	326
28	44	Roscommon Sand	36	15	19	0	70
03	21	AuGres Sand	144	29	75	58	306
04	24	AuGres Sand	181	24	84	55	344
05	23	AuGres Sand	171	33	69	54	327
22	20	AuGres Sand	173	24	75	59	331
25	40	AuGres Sand	58	7	31	11	97
33	33	AuGres Sand	64	0	77	28	169
34	30	AuGres Sand	32	0	84	0.5	116
07	46	Granby Sand	71	13	21	0.5	105
08	47	Granby Sand	41	9	122	4	176
24	44	Granby Sand	36	15	19	0	70
26	44	Granby Sand	36	15	19	0	70
27	40	Granby Sand	48	7	31	11	97
35	43	Granby Sand	51	10	26	0	87
36	46	Granby Sand	71	13	21	0.5	105
37	42	Granby Sand	55	0	115	3.2	173

* Data from Dr. Demirjian, County of Muskegon

Table 3. ESTIMATION OF THE QUANTITY OF NUTRIENTS APPLIED TO SOILS THROUGH IRRIGATION WITH WASTEWATER.

Element	Sampling Date[1]				
	June 1974	Sept. 1974	June 1975	Sept. 1975	Total Applied
	kg/ha[2]				kg/ha
N	9.1	79.0	27.6	37.4	153
P	2.3	20.5	7.0	9.8	39.6
K	13.9	121	42.7	57.0	235
Na	232	2,030	710	950	3,920
Ca	93	820	290	380	1,580
Mg	25.8	226	79.0	105	436
Zn	0.18	1.51	0.53	0.71	2.93
Mn	0.27	2.23	0.80	1.07	4.37
Fe	1.60	14.2	4.98	6.59	27.4

[1] Three background samples were collected in 1972 and 1973 prior to application of wastewater. Sampling dates indicated are for samples collected after application of wastewater.

[2] Quantity of each element applied in wastewater for the sampling period terminating on the date indicated. Data on water applied is based on circles 1, 2, 5 and 8 which received maximum water application. Data for nutrient content and water application rates from Dr. Demirjian, County of Muskegon.

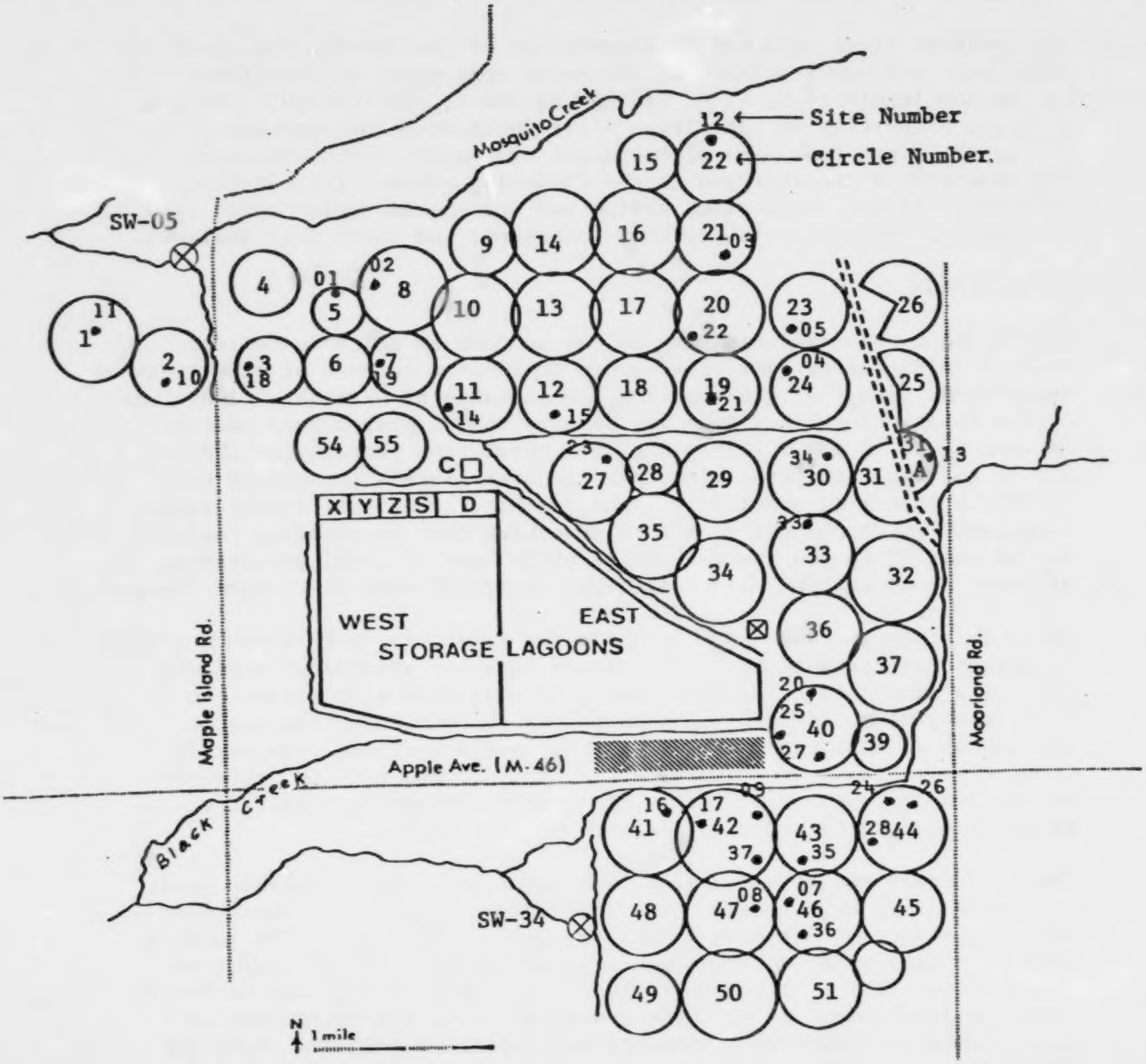
Site Number
Circle Number.
Mosquito Creek
SW-05
SW-34
Maple Island Rd.
Moorland Rd.
Apple Ave. (M-46)
Black Creek
WEST
EAST
STORAGE LAGOONS
X
Y
Z
S
D
C
N
1 mile

Figure 1. Location of sampling sites for soils (•) and outfalls (⊗).

SECTION IV

CHEMICAL ANALYSIS OF SOIL PROFILE SAMPLES

This section gives data and interpretation of the chemical analyses which were performed on each of the major soil types to establish background levels of N, P, K, Ca, Mg, Na and C, and soil pH. Changes in these properties or quantities after application of wastewater during the first two years of operation are reported and discussed. The discussions are arranged in the following order: introduction; nitrogen; calcium; magnesium, sodium and sodium adsorption ratio (SAR); phosphorus; soil pH; total carbon; potassium; and total soil analysis.

INTRODUCTION

Two types of chemical measurements may be made in soils to reflect changes in different ions or elements that occur because of some treatment—total elemental analysis and "extractable or available" fractions of the total. Total analysis may be very useful over a long period of time (i.e. 10 to 50 years) but over short time periods the changes may be too small compared with total amounts already present in soil to really determine accurately. For example, total soil K will range from 5,000 to 25,000 ppm K, but the fraction that is changing rapidly may be only 25 to 100 ppm K. On the other hand, a total measurement of heavy metal content may be adequate to detect even short-term changes.

For this study, methods have been adapted from prior soil science studies to measure extractable and/or nutrients that are available to plants and hence more active and more likely to move with soil water. In most cases, these methods are expected to reflect early changes in the status of nutrients within the soil profile. These changes, in turn, will indicate how the system is functioning, both for agronomic production and, more importantly, in nutrient removal. Individual procedures are attached as appendix I to this report.

The land treatment site contains four major soil types--Rubicon sand, Roscommon sand, AuGres sand, and Granby sand (Figure 2). These four soil types account for more than 90 percent of the area. The Rubicon sand is a very sandy well-drained soil with a thin organic layer on the surface. The clearing operation (i.e., most of this was in forest prior to development of the land treatment site) disrupted this organic layer and produced a somewhat heterogeneous surface. Both the Roscommon and AuGres sands had high water tables prior to draining. They are very sandy but have well aerated conditions in the surface soils. The Granby soils have much higher organic matter contents and have developed under high water tables. A moderate portion of these soils have been farmed in the past.

To establish baseline data for the land treatment site, eight sites were selected from within each of the major soil types by use of a soil survey map of the area and by on-site inspection. After analysis

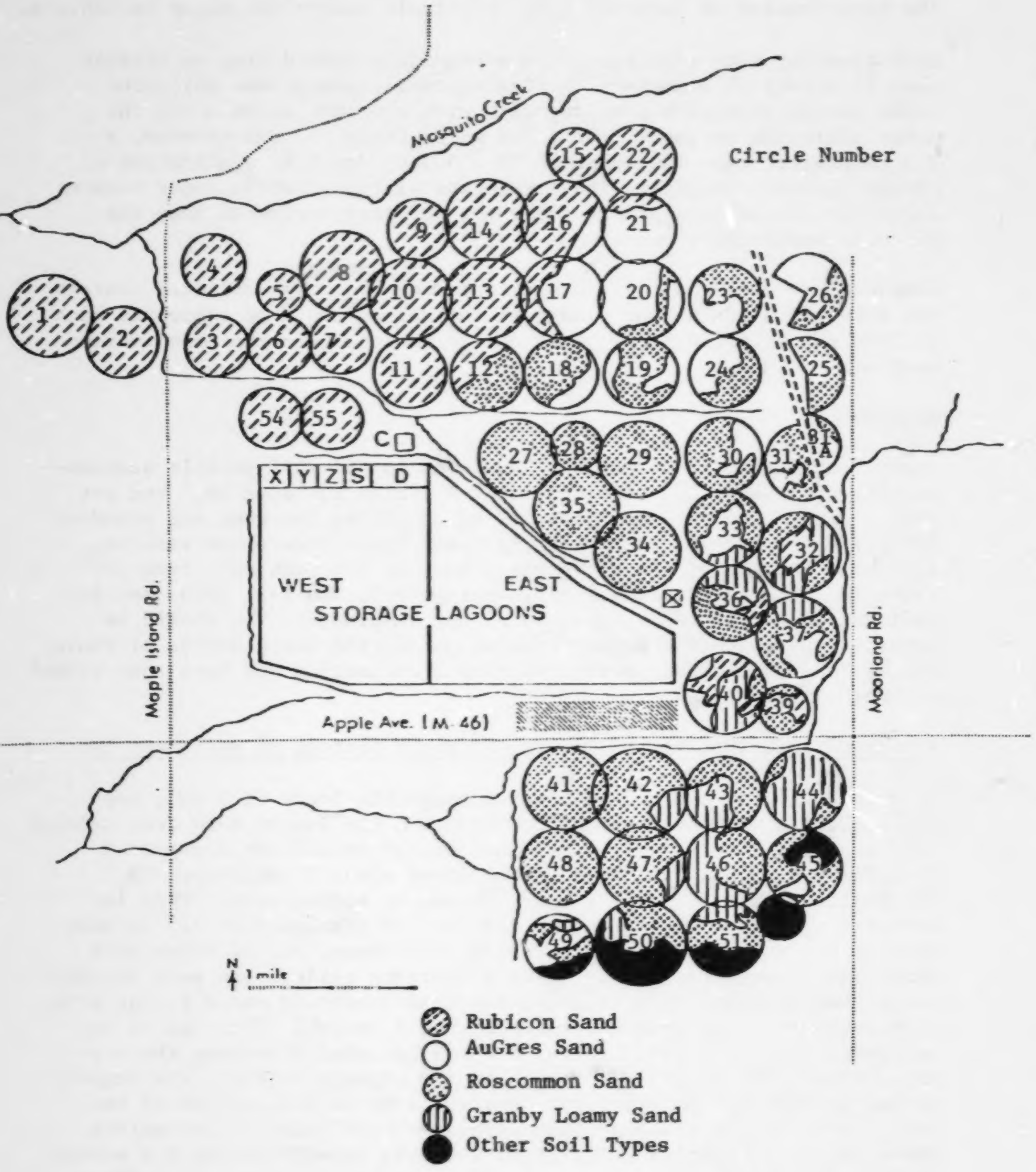
Mosquito Creek
Circle Number
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
81 A
32
33
34
35
36
37
39
40
41
42
43
44
45
46
47
48
49
50
51
54
55
C
X
Y
Z
S
D
WEST
EAST
STORAGE LAGOONS
Maple Island Rd.
Moorland Rd.
Apple Ave. (M-46)
N
1 mile
Rubicon Sand
AuGres Sand
Roscommon Sand
Granby Loamy Sand
Other Soil Types

Figure 2. Major soil types at Muskegon Wastewater Treatment site.

]

of data from the sites, one site mapped as AuGres appeared more like Roscommon; consequently, the final selections had eight Rubicon sands, nine Roscommon sands, seven AuGres sands, and eight Granby sands. The distribution of these by site and circle number are shown in Table 4.

Each sampling site consisted of a permanently marked area no greater than 15 meters in diameter. A single profile sample was collected twice yearly from each sampling site with a bucket auger until the water table was reached. After the water table was encountered, a 2.5 cm plastic tube was inserted to a 305 cm depth by application of slight vacuum. The tube with sample was withdrawn while under vacuum, carefully placed in a sampling trough, and then separated into the 15 cm (6 inch) increments.

Samples were run in a field moist state for NO_3. The moisture content was determined concurrently so that the values could be corrected back to oven dry moisture. All other determinations were run on air-dried samples.

NITROGEN

Three fractions of nitrogen were measured in the soil profile samples—soluble NO_3^-, NH_4^+, and total Kjeldahl N (which included NH_4^+ but not NO_3^-). Background data was obtained by computing the mean and standard deviation for each of the four major soil types over three sampling periods. The individual sites were combined for each soil type as shown in Table 4 for summer 1972, spring 1973, and fall 1973 sampling periods, all prior to application of any wastewater. It should be noted, however, that clearing operations and the installation of drainage systems during this period of sample collection did have some effect on the N fractions.

Effect of Soil Type on the Initial Nitrogen Content of Soil Profiles

Considering first the soluble and exchangeable forms of N (NO_3 and NH_4^+) (Tables 5 to 8), the Rubicon sand and the AuGres sand were similar in N content. The Roscommon sand had nearly double the content of both forms of N, and Granby sand contained about 6 times more NH_4^+ and 10 times more NO_3^- than either Rubicon or AuGres sand. This is somewhat reflected in the values for total N (Tables 9 to 12) in that Rubicon was much lower than AuGres and Roscommon, all of which were many times lower than Granby. The N contents reflect the soil development. Rubicon sand is a well-drained sand developed under forest with a deep water table--generally deeper than 7 meters. This led to development of a soil profile that was low in total N because the aeration caused decomposition of much of the organic matter. The organic matter present was in a relatively thin layer on the surface of the soil. Both AuGres and Roscommon were developed under a fluctuating water table. While the AuGres soil was well aerated during the summer months, the water table may have come to within 60 cm of the surface during early spring. Roscommon sand is similar, but the water table

Table 4. SITES COMBINED IN SUMMARIZING EACH SOIL TYPE

Rubicon Sand	Roscommon Sand	Augres Sand	Granby Sand
------------------	sites	-----------------	
01	09	03	07
02	13	04	08
10	15	05	24
11	16	22	26
12	17	25	27
14	20	33	35
18	21	34	36
19	23		37
	28		

Table 5. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA RUBICON SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	5.4	5.9	2.8	4.4	26	13	21	14	82	59	8	5	10.9	12.9	5.0	0.4
15-30	3.8	3.6	1.6	1.9	24	15	13	9	47	40	5	3	8.7	8.7	5.1	0.4
30-46	2.9	2.1	1.4	1.3	25	13	11	5	35	31	4	3	8.2	10.2	5.3	0.4
46-61	2.5	2.3	1.3	1.3	31	14	9	6	25	21	3	2	8.5	12.4	5.3	0.4
61-76	2.3	2.0	1.2	1.4	32	15	6	4	17	16	1	1	8.5	13.0	5.3	0.4
76-91	2.1	2.2	1.2	1.2	27	14	5	3	15	15	1	1	9.5	14.1	5.3	0.4
91-107	2.2	1.9	1.1	0.9	21	10	4	2	14	13	1	0.9	7.3	9.1	5.4	0.4
107-122	2.0	2.2	1.0	0.8	20	9	4	1	15	12	2	3	6.9	9.6	5.5	0.4
122-137	1.8	1.8	1.1	0.8	18	9	4	1	16	15	3	7	7.0	9.0	5.6	0.6
137-152	2.0	2.2	1.0	0.7	16	8	4	2	14	12	2	3	7.7	9.6	5.6	0.5
152-168	1.9	2.0	0.9	0.5	16	9	4	1	17	15	2	3	7.5	10.7	5.6	0.5
168-183	2.0	2.1	0.9	0.5	15	6	4	2	19	17	3	3	8.6	12.8	5.7	0.5
183-198	2.0	2.0	1.0	0.5	13	5	13	43	26	35	3	4	9.4	12.8	5.7	0.7
198-213	2.5	2.7	0.9	0.3	12	5	6	8	24	31	3	4	8.6	12.8	5.8	0.7
213-229	2.0	2.1	0.9	0.4	13	5	4	1	31	38	3	4	8.0	10.1	5.9	0.6
229-244	1.6	1.7	0.9	0.6	12	5	5	2	25	20	4	5	8.6	11.9	5.9	0.7
244-259	1.5	1.6	0.9	0.4	12	5	5	2	26	21	5	6	9.0	13.2	5.9	0.6
259-274	2.0	2.3	0.8	0.3	12	6	5	2	35	37	6	8	8.3	12.6	6.0	0.7
274-290	2.1	2.6	0.8	0.3	10	5	13	40	52	79	6	7	9.4	13.0	6.0	0.8
290-305	1.9	2.7	0.8	0.3	11	5	5	2	73	203	6	7	8.8	12.8	6.1	0.8

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 6. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA ROSCOMMON SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	10.0	23.3	6.0	12.4	9.6	5.8	33	23	420	430	78	150	11.0	8.9	5.6	0.7
15-30	8.7	17.9	6.9	12.3	7.9	5.6	17	10	240	240	44	110	9.2	8.4	5.6	0.9
30-46	3.8	4.4	3.1	4.3	5.6	3.9	9	7	130	140	11	13	8.0	9.1	5.8	0.9
46-61	2.8	2.3	2.3	3.0	7.2	7.0	7	4	200	580	10	15	7.5	8.7	6.0	0.9
61-76	2.4	2.1	1.5	1.0	9.1	7.7	7	3	110	210	13	29	7.5	9.2	6.0	0.9
76-91	2.5	2.4	1.3	1.4	8.4	6.8	7	4	96	83	17	34	9.4	13.1	6.2	0.9
91-107	2.3	2.0	1.4	1.7	8.6	7.3	7	4	130	230	23	48	9.6	12.5	6.2	1.0
107-122	2.8	3.2	1.4	1.7	9.0	8.2	7	4	110	110	26	49	8.6	12.0	6.3	1.0
122-137	2.1	2.2	1.0	0.5	9.2	7.9	7	4	140	230	27	50	9.9	13.4	6.2	1.0
137-152	2.3	2.2	1.2	0.6	9.6	9.0	7	4	220	460	26	52	10.5	17.8	6.2	1.1
152-168	2.4	1.9	1.0	0.4	9.2	7.8	7	6	210	420	22	48	11.1	17.2	6.2	1.2
168-183	2.6	2.4	1.0	0.6	8.9	7.1	7	7	120	230	20	44	9.0	12.2	5.9	1.0
183-198	2.1	2.0	1.0	0.4	8.2	6.0	6	5	96	130	21	49	8.6	10.9	5.7	1.1
198-213	2.1	1.9	0.9	0.4	8.9	7.4	7	5	100	140	23	52	9.3	12.1	5.7	1.1
213-229	2.5	2.4	1.0	0.4	8.3	6.7	6	3	94	140	24	50	9.4	11.4	5.7	1.1
229-244	2.1	2.0	0.9	0.4	8.0	5.7	7	5	95	140	23	44	9.6	13.4	5.7	1.2
244-259	2.6	2.2	0.9	0.3	7.5	5.4	6	4	93	120	25	45	9.5	12.8	5.7	1.2
259-274	2.5	2.3	0.9	0.3	7.3	5.9	6	3	93	120	22	40	10.1	12.3	5.8	1.1
274-290	2.4	2.5	0.9	0.3	7.7	6.3	6	4	120	180	23	39	11.0	11.8	6.0	1.2
290-305	2.7	2.9	0.9	0.3	8.0	6.2	6	3	130	180	24	41	10.3	11.9	6.1	1.2

* Mean of 9 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 7. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA AUGRES SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	4.8	8.7	3.6	5.8	11.5	12.2	32	20	310	260	49	55	14.7	14.2	5.5	0.6
15-30	2.5	3.0	2.2	2.4	7.1	10.7	21	30	210	200	37	65	13.3	14.5	5.5	0.7
30-46	2.1	2.1	1.9	2.9	5.5	5.6	9	6	100	82	20	38	11.7	13.7	5.5	0.7
46-61	2.0	2.0	1.7	2.6	7.1	6.8	6	5	67	56	8	11	10.4	12.9	5.5	0.8
61-76	2.4	4.1	1.4	1.4	9.1	6.4	5	2	51	55	6	8	10.2	14.3	5.6	0.7
76-91	1.7	2.0	1.5	2.0	11.0	9.0	6	4	61	66	8	9	12.0	14.0	5.6	0.7
91-107	1.5	1.5	1.2	1.0	10.7	8.4	5	2	47	44	6	8	9.6	12.2	5.7	0.8
107-122	1.6	1.8	1.1	0.9	11.2	7.5	5	2	54	50	9	12	11.4	14.2	5.6	0.7
122-137	2.0	2.5	1.0	0.7	10.8	7.0	5	2	50	64	7	9	9.8	12.4	5.6	0.8
137-152	1.7	2.2	1.0	0.7	11.0	6.5	8	11	43	57	8	14	9.4	11.9	5.5	0.9
152-168	1.9	1.8	1.0	0.7	12.9	6.1	5	2	32	25	7	6	10.4	11.9	5.4	0.6
168-183	2.0	2.3	1.0	0.8	10.6	5.4	5	3	45	52	8	13	9.6	11.7	5.7	1.0
183-198	1.7	2.3	1.1	0.9	10.1	5.8	5	2	43	55	10	16	9.4	10.9	5.6	0.9
198-213	1.8	2.4	1.2	1.0	10.4	6.5	5	2	40	47	10	15	9.6	10.6	5.5	1.0
213-229	2.0	2.9	1.0	0.7	10.1	6.6	5	3	86	161	8	10	8.5	11.4	5.7	1.0
229-244	1.7	2.6	1.0	0.7	10.0	8.3	5	2	130	280	8	7	8.4	11.5	5.8	1.2
244-259	1.9	2.7	1.0	0.8	10.0	8.8	6	4	120	280	8	7	8.8	11.7	5.8	1.1
259-274	2.0	3.1	1.0	0.9	9.5	7.7	8	11	140	290	11	12	9.1	12.1	6.0	1.1
274-290	1.9	2.8	1.1	1.2	9.1	7.0	6	2	100	190	16	22	8.8	10.8	5.9	1.0
290-305	1.9	3.4	1.1	1.2	8.6	7.0	7	5	170	290	16	27	9.1	11.0	6.2	1.1

* Mean of 7 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73)

** Standard deviation.

Table 8. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA GRANBY SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	39.2	80.7	34.3	80.2	17.8	16.9	84	69	1970	1830	210	450	21.3	12.4	6.4	0.8
15-30	10.6	19.8	18.6	41.4	7.8	6.9	37	31	1920	2650	190	430	21.4	17.7	6.3	0.7
30-46	3.9	6.3	8.1	17.1	4.9	4.2	17	12	1230	1680	140	330	15.7	14.4	6.4	0.9
46-61	2.5	2.5	3.1	3.3	5.1	5.2	13	11	770	1100	110	340	12.5	10.9	6.6	0.8
61-76	2.5	4.8	2.4	2.2	5.1	4.2	10	4	565	880	110	340	10.9	8.8	6.6	0.8
76-91	1.6	1.6	1.7	1.1	5.9	4.3	10	7	440	680	110	410	9.2	8.3	6.4	1.2
91-107	1.9	2.0	1.5	0.9	6.5	4.4	9	4	390	680	110	400	7.6	5.8	5.8	1.6
107-122	1.3	1.3	1.2	0.6	8.0	5.4	7	3	340	660	100	390	7.1	6.0	5.1	1.7
122-137	1.6	2.3	1.3	0.6	7.0	4.4	8	4	330	700	100	390	7.1	5.0	5.2	1.8
137-152	1.6	2.0	1.3	0.7	6.8	4.3	7	3	360	700	110	390	7.1	5.1	4.9	1.8
152-168	1.2	1.2	1.3	0.8	6.9	3.6	7	3	335	640	100	360	7.8	9.3	4.9	1.9
168-183	1.1	1.4	1.2	0.6	7.2	3.8	6	3	320	655	93	340	7.2	5.7	4.7	1.8
183-198	1.0	1.1	1.3	0.9	7.4	3.8	6	3	310	616	86	310	7.7	7.0	4.7	1.9
198-213	1.0	1.1	1.3	0.9	6.8	3.7	5	2	300	600	91	350	6.8	5.0	4.7	1.9
213-229	1.1	1.3	1.2	0.7	6.3	3.9	5	2	340	590	94	320	7.6	8.4	6.0	2.1
229-244	1.0	1.1	1.2	0.5	6.6	4.2	6	4	295	560	92	320	6.4	4.0	5.2	2.0
244-259	1.5	2.5	1.1	0.4	6.7	4.9	5	3	320	580	90	320	7.4	7.1	5.4	1.8
259-274	1.3	2.0	1.2	0.5	6.0	4.5	6	3	335	540	100	340	7.2	5.0	5.6	1.8
274-290	1.3	2.1	1.1	0.5	6.4	4.5	6	4	310	530	91	310	7.4	5.5	5.5	1.8
290-305	1.4	2.6	1.1	0.6	6.3	4.5	6	2	340	590	100	320	6.9	4.8	5.6	1.8

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 9. MEAN AND STANDARD DEVIATION FOR TOTAL NUTRIENTS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA RUBICON SAND.

Depth	N		C		P		K		Ca		Mg		Na	
	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm														
0-15	490	160	.93	.31	280	140	9700	3400	1800	1000	870	420	3560	1690
15-30	280	67	.49	.26	240	110	9400	3300	1800	1000	870	410	3730	1810
30-46	180	57	.39	.21	220	130	10200	3200	1800	900	990	630	3840	1920
46-61	130	41	.21	.13	200	90	10000	2900	1700	800	850	330	4220	1890
61-76	92	31	.15	.14	160	62	9200	2600	2000	1100	900	340	4120	2020
76-91	71	43	.21	.19	140	52	9500	3000	2100	1500	860	520	4130	1820
91-107	56	24	.15	.20	130	47	9700	2800	1800	800	1110	1640	4290	2550
107-122	51	25	.14	.14	130	60	9100	2500	2100	1400	1030	640	4830	2950
122-137	42	20	.16	.18	110	40	9300	2500	2000	1600	860	640	4200	2020
137-152	35	18	.15	.16	110	43	13100	18100	1900	1300	810	390	4780	2580
152-168	44	18	.14	.17	160	180	9800	1700	2100	1100	960	390	5530	4780
168-183	34	13	.14	.15	110	73	8800	3100	2200	1400	910	400	4710	2070
183-198	33	19	.12	.11	91	37	8500	2900	1900	1000	810	380	4620	3060
198-213	32	19	.09	.10	97	42	18800	50600	1900	1100	750	310	4850	3680
213-229	30	16	.16	.21	98	44	8600	2300	2200	1400	870	410	4540	2200
229-244	34	27	.11	.13	110	66	8700	2100	2200	1300	970	720	5270	3530
244-259	32	21	.11	.09	100	49	8700	2300	2400	1200	860	380	5530	3130
259-274	31	14	.12	.11	100	48	9100	2700	2600	1700	1000	700	4710	2100
274-290	29	12	.11	.13	99	39	9000	2900	3100	1800	1000	520	4960	3420
290-305	31	18	.11	.12	93	46	8900	2500	3300	3300	1270	1530	4460	1680

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 10. MEAN AND STANDARD DEVIATION FOR TOTAL NUTRIENTS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA ROSCOMMON SAND.

	N		C		P		K		Ca		Mg		Na	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm													
0-15	990	440	1.48	.46	190	120	8800	2400	2700	1700	780	590	3420	1720
15-30	610	370	.97	.66	160	110	10100	2400	2500	2000	600	386	3690	1600
30-46	220	170	.61	.69	150	150	10200	2500	2400	1300	660	326	4160	1790
46-61	100	52	.37	.28	95	35	10700	2900	2700	1700	880	830	4050	1410
61-76	89	86	.31	.19	92	26	10600	2700	2600	2400	830	750	4410	1620
76-91	61	25	.29	.18	100	43	10800	3100	3300	3300	950	1000	4890	3140
91-107	48	24	.28	.17	110	57	10900	3100	3100	2800	970	1080	3650	2550
107-122	50	29	.30	.21	110	70	11000	2800	3600	3200	1130	1080	4560	2440
122-137	39	13	.26	.21	100	53	12000	4500	3300	2300	1350	1780	4480	1830
137-152	36	12	.24	.18	100	50	10300	3000	4100	3300	1490	1780	3880	1250
152-168	34	14	.24	.20	110	79	9700	3700	3300	2300	1160	1100	4010	2550
168-183	31	9	.20	.17	100	48	11100	2600	3000	1800	950	820	4320	1540
183-198	28	9	.21	.16	110	46	10100	2500	2700	1700	980	920	3730	1270
198-213	26	11	.20	.17	97	42	9800	2000	3100	2000	970	790	3880	1270
213-229	30	21	.20	.16	100	51	11100	2700	3600	2700	1110	990	4140	1330
229-244	32	24	.18	.19	94	40	9900	2700	3400	2500	1140	1130	3940	1700
244-259	27	14	.18	.14	100	57	9700	3000	3500	2400	1280	1140	3700	1470
259-274	26	11	.19	.17	100	59	13100	17300	3900	3200	1540	1980	3860	1650
274-290	26	12	.20	.18	91	41	9900	3000	3900	3800	1400	1400	3680	1130
290-305	26	11	.22	.18	90	41	9700	2400	4200	4300	1500	1990	3680	1110

* Mean of 9 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 11. MEAN AND STANDARD DEVIATION OF TOTAL NUTRIENTS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA AUGRES SAND.

	N		C		P		K		Ca		Mg		Na	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm													
0-15	850	400	1.14	.36	170	100	7900	3400	1800	1000	730	430	4040	2790
15-30	540	420	.81	.45	140	87	8100	3100	2000	1400	740	500	3720	2730
30-46	280	190	.53	.33	110	42	8700	3100	2100	1100	730	480	4150	3000
46-61	150	140	.46	.39	99	39	9800	3200	2400	1300	880	750	4590	2900
61-76	120	140	.30	.23	130	140	9100	2400	2000	900	720	460	4390	2650
76-91	75	57	.26	.20	97	38	10000	2400	2500	1500	870	500	4750	2880
91-107	66	39	.22	.14	120	110	10300	2700	2100	1000	760	330	5134	3820
107-122	57	33	.22	.17	110	50	9400	2500	2600	1500	840	380	4550	2390
122-137	52	25	.21	.17	95	61	9800	2700	2000	900	790	400	4910	2170
137-152	43	23	.22	.18	180	400	9900	2500	2200	1000	800	410	5040	2360
152-168	42	17	.24	.22	110	110	9800	3000	2200	1800	880	860	4720	2190
168-183	34	16	.21	.20	170	400	9400	2100	2000	1100	820	640	4300	2220
183-198	33	21	.21	.19	95	89	10700	3300	2300	1400	930	620	6030	3470
198-213	29	17	.25	.19	84	54	9100	3600	1900	1100	820	410	4830	3130
213-229	30	13	.23	.25	79	38	9700	2700	2300	1600	990	750	4620	2590
229-244	28	12	.22	.22	80	48	9500	3000	2100	1300	940	700	4710	2600
244-259	27	13	.18	.13	85	51	9600	3000	2400	2000	840	840	5100	2760
259-274	27	10	.11	.08	77	44	9400	2900	2500	2100	960	640	5050	3220
274-290	28	10	.13	.11	91	73	10400	2700	3100	2000	1130	710	6450	5990
290-305	27	11	.15	.18	99	94	9200	2500	3300	2600	1340	1050	5860	3640

* Mean of 7 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 12. MEAN AND STANDARD DEVIATION OF TOTAL NUTRIENTS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA GRANBY SAND.

	N		C		P		K		Ca		Mg		Na	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm													
0-15	2800	1900	3.21	2.42	310	260	10100	3000	9200	11400	1300	1000	4270	1600
15-30	2120	1930	3.24	4.59	320	470	11100	2900	13400	24700	1300	900	4510	1180
30-46	1260	1610	2.14	3.95	160	140	11500	3000	15900	32800	1300	1100	5320	2740
46-61	670	900	1.51	3.06	130	63	11500	2800	11300	25700	1600	2000	5540	4030
61-76	330	440	1.05	2.69	120	60	12100	2000	7700	15400	1500	1700	4480	1510
76-91	140	130	.37	.31	110	58	11800	2200	3800	3000	1100	700	4720	1260
91-107	100	88	.32	.31	130	98	12600	3100	4300	3900	1200	1200	4970	2300
107-122	90	84	.32	.30	130	68	12300	3700	4500	4000	1400	1300	4940	1210
122-137	64	37	.28	.29	120	54	12100	3400	4500	4300	1400	1300	4490	1040
137-152	49	23	.28	.25	110	54	11400	3400	5000	5000	1400	1200	4120	790
152-168	51	23	.27	.27	120	80	11500	3500	4900	4600	1500	1500	4120	890
168-183	47	23	.26	.24	100	52	11600	3200	4800	4300	1500	1600	4310	1250
183-198	36	17	.24	.24	100	46	11900	2900	4500	4000	1300	1100	4380	1060
198-213	32	13	.22	.25	100	58	11300	3400	5000	4500	1200	1100	4250	1190
213-229	33	17	.25	.26	110	53	11700	3800	4500	3900	1300	1100	4480	1420
229-244	37	23	.25	.26	100	52	11100	3900	4500	3800	1400	1100	4050	1210
244-259	36	18	.28	.35	150	270	11700	3300	4400	3400	1400	1100	4190	1130
259-274	39	25	.28	.36	130	150	11600	3200	4700	3900	1500	1300	3940	1090
274-290	32	13	.26	.33	98	57	11100	3000	4400	4100	1400	1400	4250	1310
290-305	30	16	.26	.32	110	81	11300	3500	5500	5300	1600	1400	4240	1490

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

will be somewhat closer to the surface during the winter and spring months. The Granby soil has had a high water table--at the surface during many months of the year--unless artificial drainage has been installed. This has led to accumulation of organic matter in the Granby soil with the result of high total N and, in many cases, also high soluble forms of N.

Effect of Drainage and Farming on Nitrogen Distribution in Soil Profiles

Installation of tile drainage systems and farming these sandy soils resulted in at least two independent effects. First, draining these areas removed free water and allowed the soil profiles to be leached of soluble nutrients. Most notable was NO_3^- which moves with the water. Individual site 15 (circle 12) is an example of this effect. At the first sampling the nitrate content of the 0-15 cm (0-6 inch) layer was 9.4 ppm N as NO_3, and the 15-30 cm (6-12 inch) layer was 19.5 ppm N. All other layers in this profile were less than 1 ppm N except for the 107-122 cm (42-48 inch) and the 229-244 cm (90-96 inch) layer (2.26 and 2.51 ppm N as NO_3, respectively). By the second sampling taken during the spring of the following year, the levels of NO_3^- were less than 1 ppm N at all depths in the soil profile, indicating that the NO_3^- had been removed from the profile by leaching.

The second effect is the increased production of NH_4^+ and NO_3^- by mineralization of organic matter due to increased aeration after drainage. The best example of this occurred at site 35 (circle 43) on a Granby sand (Table 13). The NH_4^+ content was high in the 0-15 cm layer at the time of the first sampling (120 ppm N) with levels decreasing in the 15-30 cm (18.5 ppm N) and 15-46 cm (13.1 ppm N) layers. At greater depths the quantities of NH_4^+ were quite low. Nitrate N was low throughout the profile with a high value of 3.51 ppm N as NO_3 in the 0-15 cm layer. By the second sampling the following spring, the soil content of both NH_4^+ and NO_3^+ were very high in the surface layers (see Table 13). It appears that with the time between the first and second sampling, ammonification had progressed to a great degree and some nitrification had occurred. The band of higher NH_4^+ and NO_3^- at 61-76 cm suggests that the movement downward of the N had not occurred at a fast rate.

By the fall of 1973 the NH_4^+ values were lower than in the spring but still quite high. The samples collected in the spring of 1974 were very low in NH_4^+ and not really very high, comparatively speaking, in NO_3. Three possibilities exist for the removal of the large quantities of NH_4^+ and NO_3^-. First, plant uptake could account for a portion of the removal but not between fall 1973 and spring 1974. Second, leaching of NO_3^- may have occurred. This should have lead to higher values of NO_3^- in the lower horizons of the soil profile. This, in fact, occurred in the spring 1974 sampling where values as high as 5.52 ppm N as NO_3^- occurred in the soil at 290-305 cm depth. It should be pointed out that this 5.52 ppm concentration is on a dry weight basis in the soil and the solution concentration would be considerably

Table 13. AMMONIUM AND NITRATE CONTENTS OF THE SOIL PROFILE AT SITE 35 (GRANBY SAND).

	Summer 1972		Spring 1973		Fall 1973		Spring 1974	
Depth	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3
cm	ppm N							
0-15	120.0	3.5	324	96	177	59	0.6	14
15-30	18.5	2.1	71	22	31	13	*	12
30-46	13.1	1.5	29	13	12	3.0	1.2	4.9
46-61	3.4	1.6	7.7	2.6	8	1.6	*	4.1
61-76	2.5	1.5	24	8.3	2.0	1.0	1.8	2.9
76-91	1.3	1.4	3.0	1.7	2.3	0.9	0.6	3.4
91-107	5.4	1.3	6.2	1.9	3.0	0.8	1.2	1.8
107-122	1.5	1.2	2.6	1.5	2.3	0.6	*	2.1
122-137	1.4	1.8	4.7	1.8	2.7	0.6	0.6	1.6
137-152	1.0	1.8	2.4	1.4	2.0	0.6	1.8	1.8
152-168	2.2	2.0	2.6	1.2	1.5	0.6	1.2	1.7
168-183	2.6	1.3	1.8	1.4	1.8	0.6	*	2.0
183-198	1.0	1.6	2.5	1.7	1.0	0.6	2.4	2.1
198-213	1.1	1.6	1.8	1.6	.5	0.6	1.2	2.6
213-229	1.1	1.8	1.5	1.5	.8	0.5	1.8	1.8
229-244	1.2	1.8	0.9	1.3	.8	0.5	*	1.3
244-259	0.9	1.8	0.9	0.7	.5	0.5	0.3	1.3
259-274	0.8	1.8	1.8	1.1	.8	0.7	1.8	1.6
274-290	0.9	2.0	2 1	1.1	1.5	0.5	0.6	4.6
290-305	0.9	1.8	2.1	1.2	1.5	0.5	1.2	5.5

higher (probably greater than 20 ppm N as NO_3 in the ground water at this depth). The third possibility is that considerable denitrification may have occurred within this profile. This is suggested by the low values of NO_3 throughout the lower layers of the profile. This is a reasonable reaction to expect in that the NH_4^+ was being nitrified in the surface layers, the Granby sand does contain considerable organic matter which may move to the lower layers and serve as an energy source, and this soil has a high water table. But the potential does exist for movement of high quantities of NO_3^- into the ground water through this profile even without the addition of wastewater. If C diminishes in the saturated zone, the NO_3^- may no longer be denitrified and could lead to increased concentrations of NO_3^- in the groundwater.

Effect of Application of Wastewater on Nitrogen Distribution in Soil Profiles

During the initial year of operation of the system (1974) the N content of the wastewater being applied to the fields was about 2.5 ppm N as NH_4^+ and 2.5 ppm N as NO_3^- for water from the east storage lagoon and about 1 ppm N as NH_4^+ plus NO_3^- for water from the west lagoon (Demirjian, 1975). Soil profiles were collected, inasmuch as possible, after 20 cm (8 inches) of this wastewater had been applied. Mean values for these nutrients are included as tables 14 to 17. With one exception, the NH_4^+ and NO_3^- contents of the Rubicon soil profiles were reduced by the application of this water. Site number 01, however, was very high in NH_4 which is affecting the averages presented in table 14. Table 18 has been included to compare site 01 with the average of the other 7 sites. It is felt that site 01 must have been in an area where rapid ammonification was occurring due to incorporation of organic matter when preparing the site for farming operation. The application of water then moved much of this NH_4^+ into the soil profile. Although this would not be expected to happen in a soil with a large cation exchange capacity, the Rubicon sand has a very low cation exchange capacity which will allow for movement of cations in the profile. The evidence of high NH_4^+ was still present in the surface soil in September of 1974 after the application of many inches of wastewater but had virtually disappeared by the spring of 1975. The NH_4^+ and NO_3^- contents of the Roscommon and AuGres sands were low and more uniform with depth, but the Granby sand gave indications of some increased NH_4^+ and NO_3^- in the lower horizons after application of 20 cm (8 inches) of wastewater.

Means have not been calculated for the later samplings since the quantity of water that was applied to individual circles varied considerably. Thus, an examination has been made of individual sites and general conclusions drawn from this data.

After the application of rather large quantities of wastewater, the three soil types (Rubicon, AuGres, and Roscommon) appeared to stabilize and give rather uniformly low values for NH_4 and NO_3. Bands of NO_3^- were apparent in these soils at both samplings (spring and fall 1975),

Table 14. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA AFTER EIGHT INCHES OF EFFLUENT RUBICON SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	6.3	13	3.5	2.2	28	12	32	24	140	70	18	8	19.9	11.3	5.1	.4
15-30	4.4	10	1.6	1.	22	13	21	28	84	80	15	18	10.6	6.4	5.0	.4
30-46	1.2	1.7	1.2	.6	17	5	13	9	40	21	7	8	8.2	5.1	4.0	.5
46-61	5.6	14.1	1.0	.4	25	16	7	3	34	35	5	5	7.2	4.9	5.0	.5
61-76	.5	.7	.9	.4	39	13	5	2	25	35	2	3	4.8	3.4	5.9	.5
76-91	4.5	11.7	.8	.4	29	14	4	1	30	44	3	4	4.0	2.4	5.2	.5
91-107	6.2	16.7	.9	.4	22	6	3	1	15	16	2	1	3.4	2.1	5.3	.6
107-122	5.3	14.1	.8	.4	19	5	3	1	23	42	2	3	3.7	1.8	5.3	.6
122-137	.4	.3	.7	.4	18	3	3	1	15	13	1	1	3.6	2.3	5.4	.5
137-152	.3	.1	.7	.4	17	3	4	2	15	12	2	2	3.2	1.7	5.4	.5
152-168	3.8	9.8	.8	.5	16	3	4	1	19	15	3	2	3.8	2.3	5.5	.6
168-183	1.5	3.4	.7	.4	14	3	4	1	14	12	2	2	3.1	1.8	5.5	.5
183-198	1.3	2.6	.7	.4	14	4	4	2	20	18	3	4	3.2	1.5	5.6	.6
198-213	.4	.4	.7	.4	11	4	4	1	21	15	4	5	5.0	6.5	5.6	.6
213-229	1.8	4.1	.7	.3	11	4	4	3	28	26	3	4	3.9	2.6	5.6	.6
229-244	.4	.5	.6	.2	11	3	4	1	25	18	3	3	2.5	1.4	5.6	.5
244-259	.6	.5	.6	.2	10	4	4	1	44	42	6	8	4.6	3.3	5.8	.8
259-274	4.8	12.6	.7	.2	11	4	4	1	61	52	6	7	4.1	3.6	6.0	.9
274-290	5.3	14.0	1.1	.5	12.05	4	5	1	71	102	8	9	4.8	3.0	6.1	.9
290-305	1.7	3.3	1.4	1.	15.7	4	6	2	68	88	11	15	5.5	3.9	6.2	.7

* Mean of 8 sites (see Table 2).

** Standard deviation.

Table 15. MEAN AND STANDARD DEVIATIONS FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA AFTER EIGHT INCHES OF EFFLUENT ROSCOMMON SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	2.9	4.5	2.4	1.5	15	15	25	16	298	197	45	37	29.6	20.0	6.3	1.1
15-30	2.9	4.3	1.5	.8	10	8	19	18	340	279	43	28	22.2	20.4	6.2	1.1
30-46	1.0	1.1	1.0	.3	9	6	9	7	212	88	28	35	7.3	3.0	6.3	1.1
46-61	.9	1.0	1.0	.5	10	10	8	6	112	129	20	33	7.9	6.6	6.3	1.1
61-76	1.2	1.9	.9	.5	13	13	8	5	96	81	14	21	7.9	7.0	6.4	1.4
76-91	1.3	1.6	1.3	1.6	15	15	6	4	87	60	12	12	8.6	8.0	6.3	1.1
91-107	.8	.8	.8	.4	10	9	5	4	86	121	12	20	7.0	7.1	6.2	1.1
107-122	.7	.6	.8	.4	11	5	6	4	83	114	13	24	7.2	7.2	6.1	1.2
122-137	.6	.5	.8	.4	11	5	6	7	118	222	19	46	7.7	11.4	5.9	1.3
137-152	.5	.5	.8	.4	11	5	6	5	94	142	14	27	6.6	8.8	6.2	1.2
152-168	.6	.4	.8	.4	10	5	7	5	112	146	22	28	7.6	8.9	6.3	1.2
168-183	.6	.6	.6	.2	10	6	6	5	83	129	18	30	6.4	7.3	6.3	1.5
183-198	.6	.8	.8	.4	10	6	6	5	88	119	20	34	6.6	7.9	6.2	1.5
198-213	.7	.8	1.2	.8	8	5	6	5	89	112	21	36	6.5	5.4	6.1	1.7
213-229	.4	.4	1.5	1.3	7	6	7	6	100	139	24	39	6.9	8.0	6.0	1.7
229-244	1.9	3.8	1.2	.8	8	6	7	7	109	150	26	43	6.6	6.6	6.1	1.7
244-259	.5	.6	1.0	.9	8	6	8	7	104	138	26	46	6.1	5.8	6.1	1.6
259-274	.5	.5	1.0	.8	8	5	8	5	165	251	22	39	8.8	9.3	6.3	1.4
274-290	.5	.3	1.2	.9	7	5	8	5	203	330	23	41	11.6	14.2	6.6	1.3
290-305	.3	.3	1.3	1.0	7	5	8	6	196	371	26	43	12.2	12.7	6.8	1.2

* Mean of 9 sites (see Table 2).

** Standard deviation.

Table 16. MEAN AND STANDARD DEVIATION FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA AFTER EIGHT INCHES OF EFFLUENT AUGRES SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	----------	----------	----------	----------	----------	----------	----------	ppm	----------	----------	----------	----------	----------	----------	----------	----------
0-15	3.8	5.5	6.2	4.4	17	17	33	15	410	230	40	23	37.1	13.7	5.9	0.5
15-30	2.6	5.1	4.7	3.7	9	9	16	8	230	170	22	20	14.1	6.0	5.8	0.8
30-46	1.3	.7	2.9	2.2	10	7	10	7	160	200	12	10	6.6	2.3	5.8	0.8
46-61	.8	.6	2.3	1.3	10	9	6	4	140	210	9	9	4.6	2.2	5.8	0.7
61-76	.6	.5	2.1	2.0	12	9	4	3	66	69	6	6	3.8	2.0	5.8	0.7
76-91	.6	.3	2.0	1.9	10	5	4	2	53	49	5	6	3.9	2.0	5.8	0.7
91-107	.3	.4	1.6	1.3	10	5	3	1	41	33	4	3	4.0	2.2	5.8	0.7
107-122	.3	.3	1.6	1.4	12	7	4	1	31	32	3	3	5.3	3.8	5.8	0.7
122-137	.5	.5	1.5	1.2	12	9	3	2	33	25	3	3	3.7	3.1	5.8	0.6
137-152	.4	.5	1.4	1.2	15	11	4	2	44	36	3	3	6.4	8.4	6.0	0.6
152-168	.5	.3	1.6	1.4	13	8	4	2	38	27	4	3	6.8	8.5	6.0	0.7
168-183	.7	.8	1.5	1.2	13	10	4	2	33	19	4	4	6.8	9.3	5.9	0.9
183-198	.2	.2	1.7	1.5	18	14	4	2	25	19	3	3	5.1	7.8	5.7	0.9
198-213	.5	.4	1.5	1.1	14	9	4	3	25	31	3	3	5.4	8.9	5.6	0.9
213-229	.4	.4	1.4	1.2	14	10	4	2	29	26	5	8	5.6	8.2	5.4	1.0
229-244	.7	.8	2.0	1.5	13	11	4	2	30	26	5	7	5.0	6.4	5.4	1.1
244-259	.3	.3	1.9	1.4	13	11	5	3	35	28	5	8	5.6	5.9	5.4	1.1
259-274	.3	.2	2.2	1.6	12	8	4	3	47	28	9	9	5.2	7.7	5.5	1.3
274-290	.3	.3	2.2	1.4	12	8	5	3	240	490	15	14	5.5	7.0	5.6	1.4
290-305	.3	.1	2.3	1.5	11	8	6	2	280	590	17	17	7.6	8.5	5.9	1.1

* Mean of 7 sites (see Table 2).

** Standard deviation.

Table 17. MEAN AND STANDARD DEVIATION FOR EXTRACTABLE AND SOLUBLE NUTRIENT CONTENT OF SOILS FROM MUSKEGON SPRAY AREA AFTER EIGHT INCHES OF EFFLUENT GRANBY SAND.

	NH_4		NO_3		P		K		Ca		Mg		Na		pH	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm															
0-15	3.4	3.9	7.6	9.5	28	28	57	36	940	810	130	100	88.0	45.8	6.5	.7
15-30	2.0	3.3	10.7	16.7	16	22	37	30	940	880	130	110	50.8	23.2	6.1	.8
30-46	1.1	1.5	6.7	8.6	7	7	26	25	920	670	91	70	32.9	37.6	1.6	1.1
46-61	1.1	1.1	5.0	5.4	9	8	13	4	720	730	85	83	24.9	32.1	6.6	.9
61-76	1.1	.9	3.5	3.8	10	9	11	5	570	720	65	76	17.5	18.6	6.6	1.2
76-91	1.1	.7	3.2	2.8	13	14	9	5	550	690	45	56	10.4	7.3	6.6	1.4
91-107	1.0	.8	2.1	2.4	12	13	8	6	440	580	26	26	7.6	6.9	6.1	2.7
107-122	2.4	4.3	2.1	2.0	12	12	9	5	560	640	26	23	10.8	7.1	6.7	1.7
122-137	4.1	9.1	2.0	2.4	10	9	8	4	670	660	17	13	9.5	6.6	6.8	1.7
137-152	1.4	1.2	1.8	1.8	10	9	8	4	680	640	23	17	11.5	6.5	7.0	1.4
152-168	1.1	.6	1.8	1.5	8	8	8	3	630	640	28	31	12.3	6.8	7.2	1.1
168-183	.9	.7	1.6	1.2	8	8	9	4	650	700	37	45	17.3	17.0	7.0	1.3
183-198	1.7	2.0	1.9	1.8	9	8	9	4	630	680	37	45	13.9	8.8	7.0	1.4
198-213	.9	.6	1.7	1.8	9	8	8	4	510	640	14	12	11.9	8.0	6.9	1.5
213-229	1.1	.8	2.1	2.5	9	8	8	3	570	650	37	58	12.7	7.9	6.6	1.6
229-244	.8	.7	2.1	2.2	9	8	7	2	550	590	38	64	10.8	7.1	6.7	1.8
244-259	.9	.8	1.5	1.4	8	7	9	6	570	620	45	76	13.9	12.9	6.6	2.0
259-274	1.4	1.4	1.6	1.6	8	6	8	4	600	620	45	66	10.5	6.1	6.7	1.9
274-290	.9	1.0	1.7	2.0	8	6	9	4	530	550	45	63	9.8	7.4	6.7	2.0
290-305	1.1	1.1	1.7	2.5	9	6	8	5	580	580	47	68	12.8	8.8	6.7	1.9

* Mean of 8 sites (see Table 2).

** Standard deviation.

Table 18. AMMONIUM CONTENT OF SOIL FROM SITE 01.
(CIRCLE 5) AS COMPARED TO THE AVERAGE
OF THE REMAINING SEVEN RUBICON SITES

	Fourth Sampling	
Depth	Mean for Seven Sites	Site 01
cm	----- ppm N as NH_4 ------	
0-15	1.52	40.3
15-30	.75	30.1
30-46	.64	5.3
46-61	.61	40.5
61-76	.32	2.1
76-91	.24	33.5
91-107	.33	47.6
107-122	.27	40.3
122-137	.32	1.1
137-152	.32	.24
152-168	.32	27.9
168-183	.30	9.9
183-198	.39	7.6
198-213	.21	1.4
213-229	.35	11.9
229-244	.24	1.6
244-259	.45	1.7
259-274	.35	35.9
274-290	.37	40.0
290-305	.49	9.9

but the concentrations in these bands were generally low. Rubicon and AuGres contained less than 1 ppm N as NO_3^- generally, which, if converted to ppm in solution for 15% moisture in the profile, would be less than 6 ppm N in solution. The Roscommon sand did show bands of NO_3^- in the range of 3 to 5 ppm N in the soil (20 to 30 ppm N in solution at 15% moisture). Site 16 had 56 ppm N as NO_3^- between the depths of 46 and 107 cm and about 45 ppm N as NO_3^- between 213 and 244 cm in the spring 1975 samples. This was an extremely high NO_3^- content in solution. Since this concentration exceeds the quantity of NO_3^- reported in the wastewater, it suggests that the source is breakdown of soil organic matter.

The Granby sites tended to be higher in NO_3^- content. This may be attributed to two factors: 1) the high organic matter content of the surface soil is yielding NH_4^+ ions through ammonification and later NO_3^- by nitrification; 2) these sites generally have received lower applications of wastewater so they have not come to equilibrium with the NO_3^- being removed by leaching.

It must be noted here that the samplings for this study were made in early June and late September, outside of the period during which corn is actively and rapidly adsorbing NO_3^- from the soil; consequently, higher levels of NO_3^- were observed here than would be expected during July or August. Nonetheless, the concentration of NO_3^- of the Roscommon and Granby soil profiles would suggest some loss of NO_3^- at levels in solution greater than would be desired. The Rubicon and AuGres sites have lower levels. In view of the level of NO_3^- in the wastewater being applied (i.e., approximately 4.5 ppm N during the 1974 and 1975 season except when supplemented by N during the peak portion of the growing season), one must conclude that the source of the NO_3^- in the profiles from Roscommon and Granby is from the soil. This should then reduce in level as the system stabilizes. It does also suggest that the system as operated at the present time would be incapable of removing higher levels of NO_3^- if it were in the wastewater since the system was not capable of removing NO_3^- generated by the soil. Thus, one would need to look for N removal in the lagoon system or a cropping system that is capable of NO_3^- removal during a greater portion of the growing season.

CALCIUM, MAGNESIUM, SODIUM, AND SODIUM ADSORPTION RATIO (SAR)

During the first two years of operation the content of the wastewater with respect to bases was quite stable as shown in the following table.

Table 19. AVERAGE CONTENT OF WASTEWATER IN THE LAGOONS AT MUSKEGON WASTE TREATMENT FACILITY (DATA FROM DEMIRJIAN, 1975, 1976).

Nutrient	1974	1975
	ppm	
Na	115*	145*
Ca	62.5	65
Mg	16	15
K	9	10

* The 1974 figure is an average of 85 ppm Na for the west lagoon and 145 ppm for the east lagoon; the 1975 figure is an average of 125 ppm Na for the west lagoon and 164 ppm Na for the east lagoon.

This wastewater was much higher in Na than would normally be encountered in soil solution. When such wastewater is passed through a soil, by the process of cation exchange the soil will come to a stable equilibrium with respect to the exchangeable bases. If the exchangeable Na percentage becomes too high, the Na ion which is highly hydrated dispenses soil clays and organic matter, and the soil structure may deteriorate. This leads to reduced infiltration rates, poor aeration, and difficulty in management of the agronomic aspects of the system.

There have been a number of cation exchange equations used to estimate the quantity of exchange that may occur under this type of situation (see Fried and Broeshart, 1967). No single equation has proved suitable for all soil types. Exchange constants for a given soil should be determined experimentally. Sodium adsorption ratios (SAR) have been particularly useful in estimating the exchangeable Na under conditions of irrigation.

The following is an example of the calculation of SAR for 1975:

$$\text{SAR} = \frac{(\text{Na me/l})}{\left[\frac{\text{Ca me/l} + \text{mg me/l}}{2}\right]^{\frac{1}{2}}}$$

$$\text{SAR}_{1975} = \frac{\dfrac{145 \text{ mg Na/l}}{23 \text{ mg Na/me}}}{\left[\dfrac{\dfrac{65 \text{ mg Ca/l}}{20 \text{ mg Ca/me}} + \dfrac{15 \text{ mg Mg/l}}{12 \text{ mg Mg/me}}}{2}\right]^{\frac{1}{2}}} = 4.46$$

The SAR value for the water in 1975 is 4.46 which may lead to exchangeable Na percentages of 5.5 percent (USDA Handbook 60, 1954). Again it must be cautioned that the value of 5.5 is strictly an estimate and that evaluations for the particular soils in question could lead to different values. It is normally estimated that serious difficulties will arise if exchangeable Na exceeds 15%, thus 5.5 is well below this value and should give little trouble in these sandy soils.

The question may be posed, "How much Na could be allowed in the wastewater at Muskegon before serious difficulty is encountered with the agronomic aspects of the land treatment site?" The conditions that should be met for safe irrigation is an SAR less than 15 (and less than 7.5 is better) and the conductivity of the water should be less than 2,200 u mhos/cm. Using the 1975 lagoon levels for Ca and Mg an SAR of 7.5 would be reached at 260 ppm Na in the water. It is also estimated that approximately 400 ppm Na would be required to give a conductivity of the water equal to 2,200 u mhos. Using these two values, it would appear that the concentration of Na in the water could be safely increased to 260 ppm Na or even 300 (as an average rounded number). But values exceeding this should be avoided.

Cation Exchange Capacity

Cation exchange sites in the sandy soils on the Muskegon land treatment facility are expected to arise from the small amount of clay in the soils and from the organic matter in the surface layers. The clay content of these soils is extremely low; consequently, the total number of exchange sites from clay will be very low (probably less than 2 me/100 g soil unless a clay lens is encountered). On the other hand, the organic matter content of the surface soils can be quite high in certain areas, particularly for the Granby soils. Thus, the surface soil of the Rubicon may be expected to have up to 4 me/100 g soil of exchange sites from organic matter, and the Granby soils might have as high as 14 me/100 g soil of exchange sites from organic matter. Furthermore, the exchange sites from organic matter are expected to be pH dependent; consequently, the rather acid conditions, particularly for the Rubicon soil, would effectively reduce the cation exchange capacity to even lower values since the carboxyl groups, clay and organic matter, would be occupied with H^+ at pH values less than 4 to 5.

Clearing the areas and preparing the land for cultivation has led to non-uniformity of organic matter content in the surface of the soil. This may be expected to produce very heterogeneous cation exchange systems in the surface layers. The areas will become more homogeneous with time due to mixing through cultivation and to incorporation of organic residues into the surface soils.

Background Levels of Exchangeable Bases

The Na content of all soils was low and rather uniform throughout the profile (see tables 5 to 8). Except for the surface soils, the content was about 0.04 me Na/100 g soil. The only significant deviation from this quantity was in the surface soils from the Granby series which contained about double or 0.09 me Na/100 g soil.

The Mg content of the Rubicon soils was extremely low (Table 5). The mean of 8 ppm Mg would not be adequate for corn production without additional Mg. This low content is related to the very acid pH of the Rubicon sand which has developed because of coniferous forest and a well-drained sand soil which has led to the removal of Mg by leaching. This is aided by the reduced cation exchange capacity due to the acid conditions.

The Mg content of the AuGres sand soils (Table 7) is adequate for crop growth on the average with only site 22 (circle 20) being deficient in Mg. Again this low value of Mg (less than 10 ppm Mg) was associated with acid conditions.

The Mg content of the Roscommon soils (Table 6) was similar to the AuGres except for higher values in the lower layers. In the AuGres soils the average values were generally less than 10 ppm Mg below 45 cm (18 inches), but the values were generally between 20 and 30 ppm Mg in the Roscommon soils.

The Granby soils (Table 8) contained considerable Mg in the surface layers; in fact, the average was above 100 ppm Mg for all layers down to a depth of 152 cm. These soils were higher because of higher cation exchange capacities associated with higher organic matter contents and higher soil pH's in the surface layers. Furthermore, several of the Granby sites gave evidence of having received applications of dolomitic limestone in the past during a farming operation.

Changes in Exchangeable Bases with Application of Wastewater

The Na content of the soil profiles increased with increasing application of wastewater. This is illustrated in table 20 for site 01 (circle 5, Rubicon). The Na extracted by ammonium acetate was below 10 ppm in all layers of the soil prior to application of wastewater. After application of 20 cm (8 inches) of wastewater, the Na content of the surface layer was more than 20 ppm, but after the application of 380 cm (150 inches) of wastewater the Na extracted had increased throughout the entire profile. In general, water soluble Na will be much lower than the exchangeable; however, for the sandy Muskegon soils the low cation exchange capacity of the subsurface layers together with the high water content (about 15 to 20 percent moisture) makes it possible for a considerable portion of the Na to be in a water soluble form and not exchangeable.

This system is rapidly expected to overload with Na during the application of wastewater. If we assume a uniform cation exchange capacity of 2 me/100 g (perhaps high for all but the Granby soil) and a final exchangeable Na percentage of 5 percent (just slightly higher than predicted by SAR), we can predict that the profile would hold 900 kg of Na per ha.

Table 20. SODIUM, CALCIUM AND MAGNESIUM CONCENTRATIONS IN THE SOIL PROFILE OF SITE 01 (CIRCLE 5) AS A FUNCTION OF EFFLUENT APPLICATION.

Depth	Effluent Applied Cm *								
	0	20	380	0	20	380	0	20	380
cm	----- ppm Na ------			----- ppm Ca ------			----- ppm Mg ---------		
0-15	5.9	22	51	61	40	380	4.7	9.4	120
15-30	5.4	9.5	55	22	12	230	2.1	2.2	64
30-46	5.5	5.0	54	13	13	170	1.4	1.6	61
46-61	5.6	3.5	38	11	1.8	110	1.5	1.0	39
61-76	5.6	2.5	32	7	1.8	67	.5	1.0	22
76-91	4.8	2.3	25	7	1.3	44	.2	1.0	14
91-107	4.4	1.8	22	6	1.3	33	.1	0.8	7.8
107-122	4.3	3.3	21	6	2.8	33	.1	0.7	8.0
122-137	4.6	1.5	23	6	5.0	60	.4	0.7	7.6
137-152	5.6	2.0	24	6	0.9	56	.2	0.7	7.2
152-168	3.8	2.0	27	13	0.4	35	1.1	1.0	9.6
168-183	4.7	1.3	28	7	*	56	.6	0.9	6.9
183-198	5.2	2.8	23	7	22	54	.5	1.0	7.5
198-213	6.5	2.3	21	11	12	54	1.2	1.2	8.1
213-229	6.8	2.5	22	22	22	53	2.7	1.2	6.6
229-244	5.6	1.3	22	16	21	57	2.3	0.3	7.0
244-259	4.4	1.5	18	34	21	40	5.0	0.4	6.4
259-274	8.1	2.0	20	75	22	41	13	0.8	6.5
274-290	5.7	2.7	22	62	15	60	9.6	5.3	9.6
290-305	7.4	3.0	26	62	44	153	12	6.2	8.1

* 0, 8 and 150 inches, respectively.

Example of calculation:

2 me CEC/100 g (5% Na)x10 = 1 me Na/1000 g soil.
1 me Na/1000 g x 23 mg Na/me = 23 mg Na/kg soil.
1 ha = 10,000 sq meters = $1\text{x}10^8$ cm^2.
1 ha to a depth of 300 cm = 3.0 $\text{x}10^{10}$ cm^3.
Total weight of soil is 1.3 gm/cm^3 x 3.0 $\text{x}10^{10}$ = $3.9\text{x}10^{10}$ gm.
$3.9\text{x}10^{10}$x $1\text{x}10^{-3}$kg/g x 23 mg Na/kg soil x 10^{-6} kg/mg = 900 kg Na/ha.

This quantity of Na is furnished by 2.53 x 10^6 kg (5.58 million pounds) of water containing 165 ppm sodium. Consequently, an application of 60 cm (24 acre inches) would be expected to saturate the soil with Na and then to pass most of the Na directly to the drainage water. This conclusion is verified by the experimental data and suggests that much of the Na being measured in the lower portion of the profile is in fact in solution. The final consequences of this should not be serious since Na is not a real hazard to most crops at the concentration in the incoming water. Also, Na is not apparently a real pollution hazard in rivers and lakes at this concentration, but it must be emphasized that these soils will reach a rapid equilibrium with the incoming level of Na and any changes in this level will be transmitted to the drainage water after as little as 50 cm (20 acre inches) of irrigation.

Exchangeable Ca (Table 20) increased considerably in the surface layers after application of wastewater, but the relative portion of Ca to other bases decreased considerably as shown by table 20. Thus, before application of wastewater, the 0 to 15 cm layer contained .3 me Ca/100 gram soil which represented 80 percent of the .38 me bases/100 g soil. After application of approximately 380 cm (150 inches) of wastewater, the quantity of Ca had increased to 1.87 me Ca/100 grams but now was only 62 percent of the bases. This occurred because of the increase in soil pH from 5.1 to 6.6 during the application of wastewater which resulted in an increase in cation exchange capacity, most probably from dissociation of carboxyl groups associated with soil organic matter. This increase in cation exchange capacity will allow the soil to hold more exchangeable bases. As with Na, it must be concluded that after application of no more than one year's wastewater, the soil will be at equilibrium and the composition of the incoming wastewater will be very similar to the composition of the water being discharged from the drainage system. Again there should be no hazard to either agronomic crops or surface waters from this input of Ca.

The Mg content of the soils (Table 20) has rapidly increased from the deficient levels on the Rubicon soil to levels that would be adequate for crop growth as a result of wastewater application. The fraction of the exchangeable bases that was Mg increased during the application of wastewater. For example, site 01 contained 0.039 me Mg/100 grams before application of wastewater which was 10 percent of the bases; after application of 380 cm (150 inches) of wastewater, the magnesium content increased to 1.0 me Mg/100 grams which was now 33 percent of the bases. Again this is expected to stabilize at a level controlled by the ratio of Mg to other bases in the applied wastewater and should not be detrimental to agronomic crops or to surface waters.

PHOSPHORUS

Both total and Bray P1 extractable P (an index of P available to crops) have been measured in the profile samples. The background data (tables 5 to 8 and 9 to 12) were obtained by the same combination of profile samples as outlined under the N section.

Effect of Soil Type on the Initial Phosphorus Content of Soil Profiles

Rubicon sand profiles were initially moderately high in available P. This was true to a 122 cm (48 inch) depth indicating that the P content of the parent material was relatively high. The quantity of 25 ppm P in the surface soils should be adequate for agronomic crops (particularly corn) in the initial years of the operation.

Both AuGres and Roscommon sands were much lower in P initially as compared to the Rubicon profiles. The mean values of 9.6 and 11.5 ppm P for Roscommon and AuGres, respectively, may be deficient for maximum corn production during the initial years of operation. Generally speaking, wastewater should supply adequate P for growth of the agronomic crop so that this low value should not be a problem, but the wastewater being applied at Muskegon is relatively low in P and was particularly low during the first year. Consequently, it may take a few years before these soils become totally adequate for maximum crop production. But the addition of P fertilizer would not appear to be justified since that would result in shortening the number of years that the site will effectively remove P.

The Granby sand profiles have a mean value of 17.8 ppm P, but they have a much higher standard deviation. It appeared that certain of the Granby sites (for example, 07 in circle 46 and 26 in circle 41) had been previously farmed and fertilized. The level of P fell to low levels in these soils after the 30 cm (12 inch) depth. Certain of the Granby sites were very low in P initially, indicating that when they had not been fertilized, their P level was equal to or lower than AuGres or Roscommon sands.

Phosphorus Adsorption Maximum for the Major Soil Types

It was not within the scope of this project to determine or estimate the P adsorption capacity of these soils, but nevertheless, 8 samples were selected from the first sampling period and the P adsorption capacity estimated by the Langmuir adsorption isotherm (Ellis, 1973). This data is given in table 21. These sands have a moderately low P adsorption capacity. The Rubicon sand is the highest, the AuGres and Roscommon sands intermediate, and the Granby sand extremely low. It should also be noted that the AuGres sand had a very low K value (bonding energy), the sigificance of which will be discussed in a

Table 21. PHOSPHORUS ADSORPTION CAPACITY OF SELECTED SAMPLES FROM MUSKEGON WASTEWATER FACILITY.

Soil Series	Site	Depth	Adsorption* Maximum	K**	Soil Content of P @ 3 ppm P in Soil Solution
		cm	ppm	$x10^{-1}$	ppm
Rubicon	(01)	0-15	160	5.6	134
		15-30	158	25.0	151
AuGres	(03)	0-15	115	1.3	64
		15-30	175	0.3	40
Roscommon	(23)	0-15	137	5.0	113
		15-30	114	14.6	106
Granby	(24)	0-15	42	7.3	37
		15-30	23	4.3	19

*Quantity of P that will be adsorbed by the soil with maximum P in solution (as predicted by Langmuir Adsorption isotherm).

**K is a constant from the Langmuir that is related to bonding energy.

later section. With this limited number of samples it cannot be certain if the Granby sample is representative or if the adsorption capacity for P would increase in the lower horizons. Prior experience has shown that horizons high in organic matter are generally low in P adsorption capacity and that the adsorption capacity increases in the subsoil layers.

The Relationship Between Phosphorus and Agricultural Production

The levels of P needed in soils for agronomic production depends upon the yield goal or level expected. For the Muskegon area the maximum yield that should be expected is probably near 121 q/ha (150 bu/acre) for corn. This is due to very sandy, low productive soils and climate. In the initial years of operation of the site a 80 q/ha (100 bu/acre) yield goal may be more realistic. Twenty to 30 ppm extractable P would be adequate for 80 q/ha and 30 to 40 ppm P would be adequate for 121 q/ha. As pointed out earlier, only the Rubicon soils are adequate at the present time, with the exception of those soils that had a previous history of fertilization. It is expected that the P in the wastewater will increase the soil level so that in a few years all soils will be adequate.

One of the major objectives of the land treatment system is to produce clean water through nutrient removal by crops or by adsorption by land. Phosphorus removal by land treatment is an example where both methods operate. Phosphorus is first expected to be adsorbed by the soil particles, but much of this P is left in a state that is available for plant growth. Therefore, the soil may accumulate P during late fall and early spring when no crop is growing and make it available to the crop when needed. Total removal of P by a corn crop is expected to be from 16 to 25 pounds per acre (18 to 25 kg/ha) depending mostly upon final yield (See Appendix III). The quantity of wastewater necessary to supply 16 pounds of P (18 kg) will be 36 ha-cm (35 acre-inches) containing 2 ppm P; 23.7 ha-cm (23 acre-inches) containing 3 ppm P; or 17.5 ha-cm (17 acre-inches) containing 4 ppm P. Although the content of the wastewater is at the lowest level at the present time, it may likely increase to between 3 and 4 ppm P in the future. Consequently, the needs of the crop will easily be met and excess P will be supplied to the soil.

Phosphorus Adsorption by Soils after Application of Wastewater

The soils may be roughly divided into three groups based on the quantity of wastewater applied during the first two years--those receiving 50 to 178 cm (20 to 70 inches), those receiving from 254 to 330 cm (100 to 130 inches), and those receiving greater than 380 cm (150 inches). Assuming a P concentration of 2 ppm in the wastewater, the P added with the wastewater would thus vary from a low of approximately 10 pounds per acre (11kg/ha) to a high of nearly 80 pounds per acre (90 kg/ha). Due to the non-random nature of the location of the soil types, the Rubicon sands all received nearly 80 pounds of P/acre (90 kg/ha);

whereas, the Granby sites received approximately 20 pounds of P/acre (22 kg/ha). AuGres and Roscommon were intermediate, receiving averages of 43 and 35 pounds of P per acre, respectively (48 and 39 kg/ha). Therefore, it is difficult to compare the different soil types as to removal of P. A site-by-site comparison showed that 6 of the 8 Rubicon sites had accumulated P in their surface layers; one site was too variable to draw a meaningful conclusion; and one showed no accumulation. Table 22 illustrates the type of data that were obtained for the Rubicon sand profiles.

The quantity of P accumulated in the surface two layers may be estimated by the following calculation:

(1) Weight of soil in a 15 cm layer of one hectare is equal to the bulk density (1.3 gm/cm) times the volume of soil (1×10^8 sq cm/ha x 15 cm depth) = $1{,}950 \times 10^6$ gm = 1.95×10^6 kg soil/ha.

(2) P adsorbed in the 0-15 cm layer = 38-21 = 17 ppm P.

(3) $17 \text{ ppm P} = \dfrac{17 \text{ kg P}}{1 \times 10^6 \text{ kg soil}} \times 1.95 \times 10^6 \text{ kg soil} = 33.1 \text{ kg P}.$

By a similar calculation, the P adsorbed in the 15-30 cm layer is:

$$\frac{10 \text{ kg P}}{1 \times 10^6 \text{ kg soil}} \times 1.95 \times 10^6 \text{ kg soil} = 19.5 \text{ kg P}.$$

The total P adsorbed in the surface two layers would be approximately 53 kg P.

Considering that about 70 kg of P per ha were applied and that crop removal during the two years could be expected to be no more than 22 kg P per ha (since the yield was very low the first year), this balance is within experimental error and would suggest that only trivial amounts would have passed through the Rubicon sands into the drainage water.

The exception to the Rubicon data was site 12 located in circle 22. This site showed no accumulation of P. In addition, examination of the sodium data suggests that it did not receive as much wastewater as indicated in records. The reason for this is not known, but it could possibly have occurred due to non-uniform application of the wastewater on the field with higher application at locations other than that sampled. The potential effects on soil and drainage water of non-uniform application of wastewater will be discussed at a later time.

With the AuGres sites it is difficult to ascertain any accumulation of P in the profiles. Characteristically, they have increased levels of P at lower depths in the profiles in the background samples. This zone of accumulation appeared to vary in depth over rather short distances as judged by the different samplings. Table 23 gives a comparison of background P and the level after the application of approximately 380 cm (150 inches) of wastewater for site 04 (circle 24). Site 04

Table 22. INCREASE IN EXTRACTABLE P AFTER APPLICATION OF 380 cm OF WASTEWATER TO RUBICON SAND, SITE 02 (CIRCLE 8).

Depth	Extractable P	
	Background *	Fall 1975
cm	-----ppm P----	
0-15	21	38
15-30	16	26
30-46	20	18
46-61	30	19
61-76	38	44
76-91	24	34
91-107	20	21
107-122	21	17

* Mean of 1st, 2nd and 3rd Samplings from Summer 1972 through Fall 1973.

Table 23. CHANGE IN EXTRACTABLE P AFTER APPLICATION OF 380 cm OF WASTEWATER TO AUGRES SAND, SITE 04 (CIRCLE 24).

Depth	Extractable P			
	Background*	Fall 1975	Net Change	
cm	---- ppm P-----		ppm	Kg/ha-15cm **
0-15	5.8	11.3	5.5	10.7
15-30	4.1	4.4	.3	.6
30-46	4.2	6.8	2.6	5.1
46-61	7.1	10.8	3.7	7.2
61-76	14.6	5.2	(9.4)	(18.3)
76-91	16.4	5.6	(10.8)	(21.1)
91-107	11.6	14.2	2.6	5.1
107-122	10.3	22.3	12.0	23.4
122-137	12.5	15.3	2.8	5.5
137-152	12.4	13.2	.8	1.6
152-168	13.6	10.2	(3.4)	(6.6)
168-183	11.4	7.6	(3.8)	(7.4)
183-198	8.6	7.0	(1.6)	(3.1)
198-213	8.1	5.6	(2.5)	(4.9)

* Mean of 1st, 2nd and 3rd Samplings from Summer 1972 through Fall 1973.

** Assuming a bulk density of 1.3 gm/cc.

data, showing no P accumulation in the soil profile, is representative of AuGres sandy soils measured at each of the four sites (03, 04, 05, 22) receiving greater than 320 cm of water. The remaining three sites (25, 33, 34) received less than 170 cm of water and showed no accumulation of P in the soil profile. Although there is a slight increase in the P content of the surface layer, it is probably within the experimental error and in no way accounts for the approximately 50 pounds per acre of excess P (56 kg/ha) applied to this site. If the change in P is accumulated through the 213 cm depth, there is no net change suggesting that all changes are within experimental error. This must then suggest that P is moving through this profile. This may, in fact, agree with the data for the adsorption isotherms in that the bonding energy for P adsorption in the AuGres soils was extremely low, giving rise to movement at low levels of P in solution.

Life of Site for Phosphate Removal

The data is too preliminary at this time to accurately estimate the life of the site for P removal from measuring profile data, but a preliminary estimate has been made from the adsorption data. There are many management techniques that will affect the number of years that this site will remove P. The discussion below is given to stimulate consideration as to these management factors and not with the idea that the estimates are necessarily accurate. It was assumed in these calculations that effective drainage is to 152 cm (5 feet) in all cases, that water is applied at a rate of 152 cm (60 inches) per year, and that the adsorption capacity is that given in table 21. The two soils that represented the extremes in P adsorption capacity, Rubicon and Granby, were selected for examples. From table 24 it is evident the Rubicon sand is a good soil for adsorbing P, whereas the Granby adsorbs little P. With the combination of a high yield and low P input, the life of Rubicon sand in P adsorption is very long. Increasing the level of P in the wastewater added to the soil decreases the effective life of the system drastically because crop removal then no longer represents a major portion of the P removal.

One effective management practice is to increase the yield of corn. Thus, in the initial year's operation the corn was nitrogen deficient and yielded little more than 24 q/ha (30 bushels per acre), but increasing the yield to 80 q/ha (100 bushels per acre) through good management would increase the period of time that the soil would adsorb P by 25 or more percent for 2 to 3 ppm P in the wastewater. Increasing the yield to 121 q/ha (150 bushels per acre) would double the length of time that the soil would adsorb P at these levels of P input. (See Appendix III for nutrient content of corn).

The management technique of producing uneven application of wastewater by allowing it to flow freely through ends of spray bar downspouts may lead to a much shorter effective life of the system. This is illustrated in table 25 where calculations show the effect of putting all of the water on either 100, 50, or 25 percent of the soil surface.

Table 24. ESTIMATED NUMBER OF YEARS THAT P MAY BE REMOVED FROM WASTEWATER APPLIED AT 152 cm (60 INCHES) PER YEAR.

Soil Type	Yield*		P Content of Wastewater			
			2ppm	3ppm	4ppm	5ppm
	q/ha	bu/acre	------------ years††			------------
Rubicon**	24	30	115	71	52	41
	40	50	132	77	56	43
	80	100	216	100	67	49
	120	150	371	137	81	56
Granby†	24	30	12	7.5	5.5	4.3
	40	50	14	8	5.9	4.5
	80	100	23	11	7.0	5.2
	120	150	38	14	8.6	6.0

* P removed by the crop would be 7.3, 15 and 22 pounds per acre for 50, 100 and 150 bushels yield, respectively.

** The adsorption capacity for Rubicon sand is estimated to be 2,600 pounds P per acre five foot depth; after this quantity is adsorbed the level in the drainage well approached that added in the wastewater.

† The adsorption capacity for Granby sand is estimated to be 274 pounds P per acre five foot depth; after this quantity is adsorbed the level in the drainage well approached that added in the wastewater.

†† The number of years before sufficient P has been added beyond that removed by crops to equal the adsorption capacity.

Table 25. EFFECT OF UNEVEN DISTRIBUTION OF WATER ON THE EFFECTIVE LIFE OF P REMOVAL ON RUBICON SAND.

Method of distribution	Fraction of the land receiving water	P level			
		2ppm	3ppm	4ppm	5ppm
	%	- - - - - -	years*	- - - - - -	
Even	100	216	100	67	49
Uneven	50	67	39	28	21
Uneven	25	28	17	13	10

* The number of years is the time required to saturate that fraction of soil (100, 50, 24 25) with P.

Even on the Rubicon soil the effective life of the system could be shortened to 17 to 28 years if this practice were followed. The level of P that would result in the drainage water would not be as high as if the entire soil were saturated--i.e. for a 3 ppm P input level, the drainage should contain 1.5 or .75 ppm P, respectively, for 25 and 50 percent soil coverage. The result would be an increased level of P in the drainage beyond a tolerable level in a much shorter number of years.

Considering the rather drastic differences in ability to adsorb P by these soils, they should be followed rather closely by soil analyses and consideration given to applying more water to the Rubicon sand and the Roscommon sand than to the other two series.

SOIL pH

Since large volumes of wastewater will pass through the soils on the treatment site, following the law of mass action, soil pH is expected to be ultimately controlled by the pH of the wastewater applied (i.e., 7.2 to 7.4); consequently, it is of minor importance to our discussion. But the soil pH does affect certain of the chemical reactions and thus should be considered.

Background data

Initially the Rubicon sites (Table 5) were acid throughout the profile with average pH's in the surface 122 cm (4 feet) between 5.0 and 5.5, and below this depth the pH ranged from 5.5 to 6.0. The AuGres soils (Table 7) were between 5.5 and 6.2 throughout the profile. The Roscommon sands (Table 6) were slightly less acid in the surface 168 cm (5.5 feet). The Granby soils (Table 8) were much more variable, both in the surface and in the subsurface layers. First, the surface layers of some locations have evidence of a prior history of lime application. For example, site 37 (circle 42) had a pH of 7.3 in the initial sampling, but site 27 (circle 40) had a pH of 5.3 in the initial sampling. This illustrates the variation due to prior liming. A second phenomenon occurred on 6 of the 8 Granby profiles. When samples were removed and air-dried, the pH of the subsurface layers (generally from 100 to 300 cm) became very acid with pH values from 2.9 to 4.0. This is not an unusual phenomenon in soils that have been waterlogged for an extended period of time. Under reducing conditions, $SO_4^=$ is reduced to sulfide and may then accumulate if little leaching occurs. Soil pH will generally be between 6.0 and 7.0 in the anaerobic condition, but as soon as the soil is aerated, the sulfide will oxidize to SO_4 and generate H_2SO_4 which leads to very acid conditions. This is expected to be a temporary condition for two reasons: 1) soils are not stable at extremely acid conditions and Fe and Al oxides and hydroxides will decompose by combining H ions with hydroxyls to form water; this will generally lead to soil pH's between 4.0 and 5.0; 2) the addition of wastewater with pH of 7.2 to 7.4 and high levels of Ca, Mg and Na will rapidly lead to increased soil pH's as these cations replace H^+.

Changes Induced by Drainage

The greatest change induced by agronomic development was the change in aeration status that occurred with the installation of tile drainage. The acid conditions encountered in the Granby soils had disappeared from all sites except site 36 (circle 46) by the fall of 1975. Much of this change must be attributed to chemical changes in the soil that occurred because of acid dissolution of minerals, leaching of bases from surface horizons, and losses of acid materials from the subsoils through leaching.

Changes Induced by Wastewater Application

The soil pH is increasing rapidly with the application of wastewater. By fall of 1975 only six sites had pH values below 5.0 in the surface compared to 11 initially. Thirty sites had pH values greater than 6.0 by fall of 1975 compared to 9 sites initially. All sites had shown increases in soil pH except site 36 (circle 46), a Granby which had received low water application.

It was anticipated (and observed in the field---personal communication from Dr. Demirjian) that the installation of drainage in the Granby soils would lead to loss of iron in the drainage water. As previously explained, aeration of a soil that was previously waterlogged many times leads to the production of H_2SO_4. This reduces the soil pH and dissolves Fe oxides and hydroxides. The water draining from such an area will then contain Fe in either ferrous or ferric state of oxidation. Characteristically, the drainage water which is initially clear will form a white to gray colloidal precipitate upon exposure to other water with a higher pH and to the air. This precipitate will turn to yellow and then to red upon oxidation. It is expected that this effect is caused by drainage and not by application of wastewater. Once the pH of the soil profile is increased, due either to the application of wastewater or to chemical reactions within the profile, this loss of Fe should be eliminated.

TOTAL CARBON

The total C content of the Rubicon sand profiles was quite low initially, the AuGres slightly higher, the Roscommon sands about fifty percent higher, and the Granby sands were very high in organic C (0.93, 1.14, 1.48, and 3.21% C, respectively, for Rubicon, AuGres, Roscommon, and Granby). The organic matter content of the Rubicon sands decreased rapidly with depth in the 15 to 30 cm depth (6 to 12 inch), but the other soil series did not show such a dramatic decrease. The variation in total C content between samplings was very large, which is expected because of the clearing and deep discing in the initial establishing of the farming operation.

There were no obvious changes in the organic C content after application of wastewater. It would be anticipated that the Granby soils would decrease in organic matter content during the first five or ten years' operation mainly due to the increased aeration. Since the surface of the other soils was well aerated initially, they should not undergo this change. The organic matter content of the wastewater is sufficiently low that it is not expected to affect the organic C content of the soils. Application of sludge could increase the organic matter content of these soils.

Agriculturally, the Rubicon, Roscommon, and AuGres sands could benefit from additional organic matter. This suggests that applications of sludge could be quite beneficial in crop production.

POTASSIUM

Although K is not normally of concern from a pollution viewpoint, it is of importance in agronomic production and, therefore, indirectly affects the ability of a land treatment system to remove nutrients by the action of a biological filter. Also, K does move in sandy soils and, consequently, may be expected to be leached under a land treatment system.

Background Data for Potassium

Data for ammonium acetate extractable (exchangeable) K are summarized in tables 5 to 8. Rubicon sand (Table 5) was initially very low in K with only 21 ppm average in the surface soil and decreasing to less than 5 ppm in many of the subsurface layers. This level is not expected to be adequate for crop growth without supplemental K. The wastewater contains about 2.34 kg K per ha-cm (2.27 pounds/acre-inch) of effluent; therefore, an application of 150 cm (60 inches) of wastewater per year should be adequate for crop growth. Although they would still be considered low, the Roscommon and AuGres soils (Tables 6 and 7) contained about 50 percent more K in the surface than did Rubicon. Both soils were still very low in the subsurface layers. The Granby soils (Table 8) averaged 84 ppm K in the surface layers, undoubtedly reflecting a prior farming history.

Changes Induced by Wastewater Application

Table 26 summarizes changes in soil K with application of wastewater. Essentially the Rubicon, Roscommon, and AuGres soils show no change in K status after application of wastewater. This would suggest that the quantity being applied is approximately that being removed by crops or that K is being leached through the soil profile. Eighty quintal per hectare (100 bu/acre) of corn would be expected to remove 21 kg/ha (19 pounds/acre) of K (Ellis, et al. 1973). But many of the sites had received more than 140 kg (125 pounds) of K per year applied in the wastewater. Since it was not recovered in the soil, this would suggest that it was being lost in the drainage water. Data by Demirjian (1975) shows 3 and 6 ppm K in the tile and discharge water, respectively, confirming that considerable K is being discharged from the site.

Table 26. AMMONIUM ACETATE EXTRACTABLE K AT VARIOUS SAMPLING PERIODS*.

Soil Type	Depth	Sampling Period Bkg	 1974	 Spring 1975	 Fall 1975
	cm		ppm K		
Rubicon	0-15	21	32	31	22
	15-30	13	21	18	13
	106-122	7	6	7.8	4.4
Roscommon	0-15	33	25	25	29
	15-30	17	19	16	19
	106-122	7	6	7.8	4.4
AuGres	0-15	32	33	30	28
	15-30	21	16	24	20
	106-122	5	4	5.7	6.5
Granby	0-15	84	57	46	30
	15-30	37	37	30	23
	106-122	7	9	10	7

* Bkg is a average of the first three sampling periods prior to application of wastewater, 1974 is an average of locations within each soil type after 8 inches of application, and the remaining two sampling periods are an average of all sites for each soil type even though water distribution was not uniform.

Loss of the monovalent ion K in the drainage water occurs because it does not compete favorably with divalent ions, particularly Ca, for exchange sites. Thus, when wastewater is applied that contains 3.25 m.e./liter Ca but only 0.25 m.e./liter K, it is most likely that a large percent of the K will be lost by leaching.

TOTAL SOIL ANALYSIS

Total soil chemical analysis showed little change during the period of wastewater application except for changes in total N and C which were previously discussed. Thus, for the short-run time period it may be concluded that available and extractable soil chemical analyses are much more sensitive to changes induced by wastewater application than total analyses. This would suggest that these are the analyses that should be followed during the next one to three years. Nonetheless, the total chemical analysis data are valuable in establishing background levels which may be useful for long-term evaluation of the land treatment system. But it would appear that total analysis made on an every-five-year basis would be adequate to follow all changes in total nutrients except N and C.

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SECTION V

HEAVY METALS

This section gives data and interpretation of the chemical analyses which were performed on each of the major soil types to establish background levels of Fe, Mn, Zn, Cu, Pb, and Hg. Changes in the soil's content of these heavy metals after application of wastewater during the first two years of operation of the land treatment section of the Muskegon waste treatment system are reported and discussed. The discussions are arranged in the following order: general background and summary; and chelate extractable heavy metals.

GENERAL BACKGROUND AND SUMMARY

Selected total and chelate extractable micronutrients and heavy metal analyses were conducted on soil profile samples. The elements determined were Fe, Mn, Zn, Cu, Pb, and Hg on samples taken at 15 cm (6 inch) intervals down to a depth of 305 cm (120 inches) in Rubicon, Roscommon, AuGres, and Granby sands which are the main soil types on the wastewater treatment site. Samples were obtained at 8 sites on the Rubicon sand, 9 sites on the Roscommon sand, 7 sites on the AuGres sand, and 8 sites on the Granby sand (Figure 1 and Table 2).

Differences in total and chelate extractable Fe, Mn, Zn, and Cu in the Rubicon, Roscommon, AuGres, and Granby sands varied widely from sampling site to sampling site even within a soil type. However, general trends were evident, and the major differences in extractable metals were between the surface layers and points deeper in the profile. Also, major changes in extractable metal levels occurred between the background samples (first three samplings) and the final sampling taken in September 1975. The background data for extractable heavy metals is given in tables 27 to 30, and the background data for total heavy metals is given in tables 31 to 34. Table 35 has been prepared to compare the changes in extractable heavy metals in the final sampling with the baseline data at two depths, 0 to 15 cm (0 to 6 inches) and 137 to 152 cm (4.5 to 5 feet).

In general, the only metal added to the soils in appreciable quantities through the wastewater was Zn. Zinc, which may have been added in amounts up to 0.2 ppm Zn in the wastewater, did not show any total accumulation, even though more than 6 kg per ha (7 pounds per acre) of Zn could have been added to sites receiving more than 380 cm (150 inches) of wastewater. Crop removal would account for less than 0.9 kg/ha (1 pound per acre) of Zn. Therefore, Zn should be detected in the surface samples in the next few years if the level in the irrigation water is greater than 0.1 ppm Zn.

Table 27. MEAN AND STANDARD DEVIATION OF EXTRACTABLE HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA RUBICON SAND.

Depth	Fe		Mn		Zn		Cu		Pb		Hg	
	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	72	54	9	11.0	1.70	1.58	.30	.24	.23	.36	.00	.00
15-30	36	40	3.2	4.4	.59	.32	.27	.26	.14	.29	.00	.00
30-46	14	8.9	1.6	1.2	.60	.85	.22	.24	.09	.17	.00	.00
46-61	11	7.1	1.5	1.6	.27	.18	.18	.23	.07	.10	.00	.00
61-76	6.9	5.6	1.2	1.4	.23	.16	.19	.26	.07	.10	.00	.00
76-91	6.1	4.8	1.4	1.5	.26	.31	.17	.19	.07	.10	.00	.00
91-107	6.3	4.5	1.4	1.5	.24	.18	.23	.23	.09	.14	.00	.00
107-122	5.8	4.1	1.4	1.4	.21	.21	.16	.16	.07	.11	.00	.00
122-137	5.7	3.6	1.3	1.4	.23	.21	.16	.24	.07	.10	.00	.00
137-152	7	5.2	1.6	2.0	.34	.63	.19	.21	.06	.09	.00	.00
152-168	6.6	5.6	1.3	1.3	.20	.16	.24	.30	.07	.10	.00	.00
168-183	6.2	4.1	1.3	1.4	.24	.17	.21	.21	.09	.12	.00	.00
183-198	6.5	3.7	1.4	1.3	.25	.21	.15	.15	.06	.10	.00	.00
198-213	7.1	4.1	1.4	1.4	.27	.21	.17	.19	.06	.09	.00	.00
213-229	7.9	6.3	1.7	2.0	.43	.70	.17	.20	.05	.08	.00	.00
229-244	7.9	5.4	1.4	1.3	.26	.23	.22	.24	.06	.09	.00	.00
244-259	8.3	6.5	1.4	1.3	.25	.24	.23	.29	.07	.10	.00	.00
259-274	7.5	6.5	1.3	1.3	.26	.21	.22	.31	.07	.10	.00	.00
274-290	8.4	6.9	1.6	1.6	.23	.17	.20	.25	.08	.12	.00	.00
290-305	9.1	7.2	1.6	1.7	.41	.56	.22	.23	.09	.12	.00	.00

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 28. MEAN AND STANDARD DEVIATION OF EXTRACTABLE HEAVY METALS OF SOIL FROM MUSKEGON SPRAY AREA-BASELINE DATA ROSCOMMON SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	107	60	2.9	2.3	1.73	.86	.39	.22	.42	.67	.00	.00
15-30	73	48	1.7	1.3	1.08	.53	.33	.21	.24	.47	.00	.00
30-46	32	24	1.1	1.3	.61	.41	.28	.22	.07	.12	.00	.00
46-61	21	14	.9	1.2	.42	.31	.27	.21	.09	.13	.00	.00
61-76	23	29	.7	1.0	.38	.24	.26	.25	.08	.12	.00	.00
76-91	13	7	.7	1.1	.42	.35	.25	.18	.09	.15	.00	.00
91-107	14	12	.9	1.8	.40	.29	.28	.21	.07	.10	.00	.00
107-122	14	9.6	.8	1.2	.42	.38	.35	.26	.08	.12	.00	.00
122-137	16	12	.9	1.2	.48	.45	.40	.30	.07	.12	.00	.00
137-152	18	16	1.1	1.8	.50	.42	.49	.40	.07	.12	.00	.00
152-168	18	13	.9	1.1	.58	.42	.42	.36	.08	.12	.00	.00
168-183	21	15	.9	1.3	.70	.95	.31	.27	.11	.23	.00	.00
183-198	20	17	1.0	1.6	.94	.99	.32	.28	.08	.12	.00	.00
198-213	19	18	1.2	2.3	.52	.36	.32	.23	.09	.15	.00	.00
213-229	18	15	.9	1.3	.52	.34	.36	.25	.09	.18	.00	.00
229-244	14	10	.9	1.5	.48	.36	.31	.21	.07	.11	.00	.00
244-259	18	12	1.1	2.0	.50	.35	.32	.26	.08	.15	.00	.00
259-274	15	9.6	1.0	1.7	.56	.62	.31	.21	.07	.09	.00	.00
274-290	14	10	1.0	1.4	.48	.37	.33	.27	.06	.10	.00	.00
290-305	14	14	1.2	2.1	.50	.38	.37	.26	.06	.09	.00	.00

* Mean of 9 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 29. MEAN AND STANDARD DEVIATION OF EXTRACTABLE HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA AUGRES SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	77	43	2.9	2.1	2.06	1.30	.42	.56	.94	1.42	.00	.00
15-30	47	31	2.2	4.4	1.27	1.76	.23	.22	.19	.26	.00	.00
30-46	27	19	1.5	2.8	.64	.47	.19	.21	.15	.21	.00	.00
46-61	27	29	.9	1.4	.43	.25	.16	.17	.10	.12	.00	.00
61-76	25	25	.9	1.4	.64	.72	.15	.17	.11	.13	.00	.00
76-91	28	18	.9	1.5	.52	.31	.15	.21	.11	.13	.00	.00
91-107	23	15	.9	1.4	.53	.54	.14	.14	.10	.12	.00	.00
107-122	28	37	.9	1.4	.44	.38	.25	.25	.10	.13	.00	.00
122-137	29	40	.8	1.4	.48	.29	.21	.21	.18	.32	.00	.00
137-152	26	24	.9	1.4	.54	.31	.22	.18	.13	.18	.00	.00
152-168	22	23	.9	1.4	.46	.25	.20	.18	.13	.18	.00	.00
168-183	18	18	.9	1.4	.41	.30	.22	.21	.11	.15	.00	.00
183-198	22	18	.8	1.5	.49	.31	.20	.17	.10	.15	.00	.00
198-213	23	19	.9	1.4	.48	.35	.23	.21	.13	.19	.00	.00
213-229	23	18	.9	1.5	.63	.40	.22	.20	.13	.16	.00	.00
229-244	22	16	.9	1.4	1.40	2.35	.24	.22	.15	.18	.00	.00
244-259	21	15	.9	1.4	.50	.25	.24	.21	.16	.19	.00	.00
259-274	21	13	.9	1.5	.61	.35	.16	.15	.13	.22	.00	.00
274-290	22	15	.9	1.5	.62	.35	.16	.13	.11	.13	.00	.00
290-305	23	18	.9	1.4	.64	.46	.19	.16	.14	.22	.00	.00

* Mean of 7 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

**Standard deviation.

Table 30. MEAN AND STANDARD DEVIATION OF EXTRACTABLE HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA GRANBY SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm						ppm						
0-15	163	158	2.8	3.3	3.08	1.74	.47	.66	.62	.87	.00	.00
15-30	123	78	1.6	1.7	2.43	3.53	.43	.35	.61	1.00	.00	.00
30-46	82	64	1.2	1.4	.81	.56	.36	.25	.33	.45	.00	.00
46-61	76	98	1.2	1.9	.80	1.01	.40	.31	.38	.87	.00	.00
61-76	74	98	1.1	1.7	.69	.70	.45	.36	.36	.73	.00	.00
76-91	72	58	1.1	1.7	.59	.35	.46	.39	.24	.40	.00	.00
91-107	87	60	.9	1.1	.64	.39	.40	.39	.23	.41	.00	.00
107-122	106	85	.9	1.1	.65	.41	.48	.36	.24	.41	.00	.00
122-137	85	62	.9	1.1	.97	.84	.38	.34	.22	.41	.00	.00
137-152	85	58	.9	1.1	.76	.35	.41	.42	.21	.41	.00	.00
152-168	93	80	1.0	1.0	.84	.50	.46	.41	.25	.43	.00	.00
168-183	95	73	.9	1.1	1.16	.83	.44	.35	.23	.40	.00	.00
183-198	85	67	.9	1.2	1.12	.71	.40	.30	.23	.43	.00	.00
198-213	81	69	1.1	1.1	1.07	.62	.32	.28	.20	.40	.00	.00
213-229	71	59	.8	1.0	.99	.52	.40	.34	.21	.41	.00	.00
229-244	69	51	.9	1.0	.94	.44	.41	.40	.21	.40	.00	.00
244-259	64	50	.9	1.1	.91	.58	.35	.34	.32	.64	.00	.00
269-274	55	51	.8	1.0	.92	.58	.39	.36	.20	.40	.00	.00
274-290	61	45	1.0	1.1	1.00	.60	.42	.36	.26	.51	.00	.00
290-305	54	43	.8	1.1	1.13	.83	.46	.40	.21	.41	.00	.00

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 31. MEAN AND STANDARD DEVIATION OF TOTAL HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA RUBICON SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm						ppm						
0-15	4200	1300	170	90	35	17	25	40	.7	.9	.3	.4
15-30	4100	1300	110	56	33	19	22	34	.7	.9	.4	.5
30-46	4300	1300	82	25	27	10	22	39	.7	.9	.3	.3
46-61	4200	1300	75	24	24	9	22	42	.7	.9	.4	.4
61-76	3600	1100	60	24	22	11	20	38	.7	.9	.3	.3
76-91	3300	1200	60	25	18	10	18	37	.7	.9	.4	.4
91-107	3500	1500	69	32	18	10	20	40	.7	.9	.5	.5
107-122	3300	1300	60	26	18	9	20	38	.7	.9	.2	.0
122-137	2800	900	59	29	15	10	20	44	.7	.9	.2	.0
137-152	2900	900	51	16	15	11	24	53	.7	.9	.2	.0
152-168	3100	1100	59	21	17	10	24	59	.7	.9	.3	.3
168-183	3200	1300	60	25	18	11	23	45	.7	.9	.3	.3
183-198	3000	1200	66	39	32	69	21	45	.7	.9	.2	.0
198-213	3100	1100	60	23	19	23	20	44	.7	.9	.2	.0
213-229	2600	1300	68	35	20	21	19	35	.7	.9	.2	.0
229-244	3100	1600	65	36	23	23	20	39	.7	.9	.2	.0
224-259	3000	1200	66	36	26	32	21	43	.7	.9	.2	.0
259-274	3200	1600	65	26	26	48	24	55	.7	.9	.3	.3
274-290	3400	1600	62	26	22	23	20	46	.7	.9	.2	.0
290-305	3400	1500	63	30	46	35	20	41	.7	.9	.2	.0

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 32. MEAN AND STANDARD DEVIATION OF TOTAL HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA ROSCOMMON SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	4200	2400	71	73	22	9.4	14	13	.7	.9	.4	.5
15-30	4200	2700	59	39	17	10	13	12	.7	.9	.2	.0
30-46	3700	2000	51	31	15	9.1	13	15	.7	.9	.2	.0
46-61	3300	1600	55	26	14	7.2	11	18	.7	.9	.2	.0
61-76	2600	950	54	24	16	9.6	11	18	.7	.9	.2	.0
76-91	2600	1200	56	20	15	9.0	8.4	10	.7	.9	.2	.0
91-107	2500	1100	54	27	20	16	9.0	10	.7	.9	.2	.0
107-122	2600	1100	59	31	17	10	9.7	10	.7	.9	.3	.2
122-137	2600	1300	58	25	15	8.5	8.2	9.9	.7	.9	.2	.0
137-152	2700	1400	61	30	17	8.6	9.5	12.9	.7	.9	.3	.2
152-168	2800	1300	56	26	19	12.4	9.3	11	.7	1.0	.3	.3
168-183	2500	1100	55	28	18	13	7.7	10	.7	.9	.2	.0
183-198	2300	990	49	20	16	12	8.5	10	.7	.9	.2	.0
198-213	2300	990	48	24	15	6.3	8.2	11	.7	.9	.2	.0
213-229	2500	940	41	30	15	6.1	10.2	12	.7	.9	.3	.3
229-244	2500	980	50	36	19	14	8.5	10	.7	.9	.3	.3
244-259	2800	1300	53	38	16	8.0	8.2	9.1	.7	.9	.2	.0
259-274	2700	1300	66	44	34	100	8.0	10	.7	.9	.2	.0
274-290	2400	990	52	30	14	7.9	7.7	10	.7	.9	.2	.0
290-305	2400	990	53	24	13	6.5	8.4	11	.7	1.0	.2	.0

* Mean of 9 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 33. MEAN AND STANDARD DEVIATION OF TOTAL HEAVY METALS OF SOILS FROM MUSKEGON SPRAY AREA-BASELINE DATA AUGRES SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	3000	2800	60	34	25	17	15	24	.9	1.0	.4	.5
15-30	2800	2400	53	25	28	29	16	23	.9	1.0	.2	.2
30-46	2600	1900	49	26	19	13	13	25	.9	1.0	.3	.2
46-61	2900	1500	68	33	18	15	13	25	.9	1.0	.4	.6
61-76	2400	970	47	26	20	13	16	25	.9	1.0	.2	.2
76-91	2400	830	54	24	19	16	12	26	.9	1.0	.2	.2
91-107	2400	820	50	22	23	24	16	27	.9	1.0	.4	.3
107-122	2500	880	51	17	22	22	16	29	.9	1.0	.4	.4
122-137	2400	910	50	19	18	16	13	20	.9	11.0	.3	.2
137-152	2400	1100	50	15	19	15	8.2	9.1	.9	1.0	.2	.2
152-168	2400	990	46	27	21	22	11	12	.9	1.0	.4	.4
168-183	2400	1700	39	24	19	11	9.1	12	.9	1.0	.3	.3
183-198	2400	1100	50	29	17	13	12	18	.9	1.0	.2	.2
198-213	2100	690	42	25	26	22	9.6	13	.9	1.0	.4	.3
213-229	2100	980	43	24	17	14	10	11	.9	1.0	.3	.2
229-244	2000	910	42	22	17	14	9.5	13	.9	1.0	.2	.2
244-259	2600	1700	39	18	19	15	10	14	.9	1.0	.4	.7
259-274	2300	900	37	16	20	14	7.8	10	.9	1.0	.4	.3
274-290	2300	660	43	25	19	14	9.3	12	.9	1.0	.2	.2
290-305	2600	1200	42	15	18	13	8.5	11.9	.9	1.0	.3	.3

* Mean of 7 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 34. MEAN AND STANDARD DEVIATION OF TOTAL HEAVY METALS OF SOIL FROM MUSKEGON SPRAY AREA-BASELINE DATA GRANBY SAND.

	Fe		Mn		Zn		Cu		Pb		Hg	
Depth	$\bar{x}$*	SD**	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD	$\bar{x}$	SD
cm	ppm											
0-15	4800	2100	95	46	40	29	12	12	1.2	1.0	.2	.2
15-30	4600	2300	91	58	37	31	15	16	1.2	1.0	.2	.2
30-46	3500	2200	86	73	32	26	11	13	1.2	1.0	.2	.2
46-61	3000	1300	76	75	25	22	8.0	9.3	1.2	1.0	.2	.2
61-76	3000	1200	59	56	29	31	8.5	12	1.2	1.0	.2	.2
76-91	2600	660	52	23	21	19	5.6	7.2	1.2	1.0	.3	.4
91-107	3100	1100	60	34	22	19	5.2	9.6	1.2	1.0	.3	.2
107-122	2900	910	63	31	23	19	6.1	10.9	1.2	1.0	.4	.5
122-137	3200	1400	75	43	25	26	5.3	8.3	1.2	1.0	.3	.5
137-152	2900	1200	66	38	22	22	6.4	9.3	1.2	1.0	.3	.4
152-168	2700	650	55	27	23	21	7.1	14	1.2	1.0	.2	.2
168-183	2700	960	52	33	24	21	8.6	16	1.2	1.0	.3	.5
183-198	3000	1200	58	26	23	22	6.0	8.6	1.2	1.0	.3	.4
198-213	3300	1800	58	32	24	23	8.2	14	1.2	1.0	.4	.6
213-229	2900	1000	52	27	27	25	7.1	14	1.2	1.0	.4	.5
229-244	2900	1400	52	30	27	25	9.5	18	1.2	1.0	.2	.2
224-259	2800	850	52	26	23	20	8.4	13	1.2	1.0	.3	.2
259-274	2700	840	50	25	27	28	9.0	15	1.2	1.0	.3	.2
274-290	2700	850	47	23	25	25	6.1	9.3	1.2	1.0	.3	.2
290-305	2900	1200	54	31	22	19	6.6	8.9	1.2	1.0	.4	.5

* Mean of 8 sites (see Table 2) and 3 sampling dates (7/72, 6/73 and 9/73).

** Standard deviation.

Table 35. CHANGES IN CHELATE EXTRACTABLE Fe, Mn, Zn and Cu AFTER APPLICATION OF WASTEWATER.

Chelate Extractable Metal	Sampling* Period	Soil Type and Depth							
		Rubicon		Roscommon		AuGres		Granby	
		0-15cm	135-150cm	0-15cm	135-150cm	0- 5cm	135-150cm	0-15cm	135-150cm
		ppm							
Fe	Bkg	72	7	107	18	77	26	160	85
	Sept. 1975	17	4	22	14	26	11	20	16
Mn	Bkg	10	1.6	2.9	1.1	3.0	0.9	2.8	0.9
	Sept. 1975	1.5	0.4	2.1	0.4	0.7	ND	1.5	0.2
Zn	Bkg	1.7	0.3	1.7	0.5	2.1	0.5	3.1	0.8
	Sept. 1975	1.2	0.1	1.4	0.3	0.8	0.3	1.8	0.1
Cu	Bkg	0.3	0.2	0.4	0.5	0.4	0.2	0.5	0.4
	Sept. 1975	ND	ND	ND	ND	ND	ND	ND	ND

* Bkg is an average of the three sampling periods prior to application of wastewater.

ND is less than .2 ppm for Mn and Cu.

CHELATE EXTRACTABLE HEAVY METALS

Chelate extractable Zn, Cu and Mn have been measured in soils to estimate that fraction of these heavy metals that are available for plant uptake. Thus, this measure has been used here to estimate the fraction of heavy metals which may be susceptible to incorporation into our food chain. It is also probable that this fraction would be more susceptible to movement in soils than would precipitated forms of the heavy metals.

Levels of chelate extractable heavy metals were much higher in the surface horizons than in the subsurface layers. This strong association with soil horizons that were high in organic matter is to be expected.

The most noticeable effect of operation of the system was the reduction in chelate extractable heavy metals, particularly Fe and Mn, by the time of the seventh sampling in September 1975. For example, extractable Fe decreased from 72 to 17 ppm for the Rubicon sand, and the other soils were comparable. A large part of the extractable Fe was probably associated with organic matter. When the land was drained, placed under cultivation, and irrigated, the organic matter was mixed by implements and generally handled in a manner which resulted in its decomposition. This reduced the soil's ability to maintain the Fe in a soluble or extractable form. The pH of the applied wastewater was about 7.2 which resulted in increases in the soil pH (see Section IV). This is expected to result in precipitation of the heavy metals, particularly Fe and Mn, in the pH range of the soils at the Muskegon site.

There was no evidence of accumulation or movement of heavy metals in the soils even after application of 380 cm (150 inches) of wastewater. This would indicate that the site should operate effectively in heavy metal removal for more than 50 years at the present rate of input.

SECTION VI

SOIL PHYSICAL PROPERTIES

STUDY SITES

This section gives data and interpretation of physical properties of the soils at the Muskegon land treatment site which may be important to application of wastewater. A discussion of the changes in physical properties of the soils after application of wastewater is included. The discussions are arranged in the following order: study sites; methods of study; results and discussion; and addendum.

Originally nine study locations were selected. These included sites which were thought to be characteristic of each of the four main soil series on the project. These included AuGres, Granby, Roscommon, and Rubicon soil series. Two sites were selected for each series. They were selected so that they would occur in different irrigation circles and in large areas of occurrence of the soil series. The sites also had to be accessible for the infiltration equipment. AuGres sites were selected on circles 23 and 40, Granby sites on circles 46 and 47, Roscommon sites were on circles 42 and 48, and Rubicon sites were on circles 3 and 5. Initially there was a finer-textured Granby on circle 42 which was thought to be interesting to study; however, after the first year it was evident that this site was covered with a silt fill, was actually not a natural soil, nor was it a major component of the project. Therefore, the Granby with silt fill, which was studied the first year on circle 42, was abandoned the following year. After the first year and the initiation of the water spreading, the Roscommon site on circle 48 was no longer accessible; therefore, a new site was selected on circle 50.

METHODS OF STUDY

Infiltration

Infiltration measurements were made in the field, using concentric ring infiltrometers with rings of 12.5 and 22.5 cm (5 and 9 inch) diameter. The measurements were replicated ten times on the surface soil and five times on the subsoil. The rings were driven 2.5 to 5 cm (1 to 2 inches) into the surface of the top soil or subsoil after excavation for the measurement. Using large automatic burets set at 2.5 cm (1 inch) above the surface of the soil, water was measured as it infiltrated the center 12.5 cm (5 inch) ring. The outside ring was maintained at the same water level with a constant water level device. Infiltration measurements were made at 5-minute intervals for the first half hour, ten-minute intervals for the second half hour, and at 15-minute intervals for the next four hours, for a total infiltration time of 5 hours. The average of the first hour is considered the initial dry infiltration rate. The average infiltration rate for the last hour is considered the minimum dry infiltration rate. Soil was allowed to drain naturally from 12 to 18 hours, and then the wet infiltration run was performed in the same manner for an additional five hours. The initial wet is the first hour's infiltration, the minimum wet is the fifth hour infiltration. Before the initial dry infiltration, moisture samples were taken and are recorded with the infiltration analyses.

Mechanical Composition

Mechanical composition was determined by the Bouyoucos Hydrometer Method. Fifty grams of soil was dispersed by adding 100 ml of a 5% hexametaphosphate solution and water and then stirring on a mixer dispersing unit for 5 minutes. The two-hour hydrometer reading was used as the measure of clay. The dispersed sample was then washed through a 325-mesh sieve. The total sands were dried and weighed. The dry sands were split to one-quarter with a sample splitter and dry sieved with standard sieves on a sieve shaker for 15 minutes.

Hydraulic Conductivity and Soil Water Characteristic

Soil cores were collected at the site of the infiltration determination, using 7.5 cm (3 inch) diameter, 7.5 cm (3 inch) long cylinder, and a standard hand driven core sampling apparatus. These samples were taken of the surface 3 inches, which was entitled A_p, of the B horizon, and of the underlying material which was designated as C. These samples were taken with ten replications packed in individual cartons and transported to the laboratory. In the laboratory, samples were covered on the bottom with a sheet of filter paper which was held in place by cheesecloth and a rubber band. The samples were saturated with water for a period of several days, and then the other analyses were performed.

Cylinders (2.5 cm (one inch) deep) were attached to the core samples, and the saturated core sample was placed on a Buckner funnel with 1.25 cm (1/2 inch) of water applied at a constant head using a Mariott bottle to maintain the water level. The amount of water which drained from the sample for one-half hour was measured and the hydraulic conductivity calculated.

The saturated samples were then weighed and placed on a series of blotting paper tension tables adjusted to 0.01 atmosphere, 0.02, 0.03, 0.04 atmospheres of tension. Samples were allowed to equilibrate for two days, weighed, and moved to the next tension. From there, the samples were placed in a pressure plate apparatus and weighed after a 2-day equilibrium at 0.1, 0.33, and 1.0 atmospheres pressure. After this, the samples were oven dried and reweighed. From this data, the soil water characteristics from saturation to one atmosphere were calculated on a percent water-by-volume basis. Bulk density was calculated from the oven dry weight and volume of core. Pore space was calculated using the saturated water loss.

Aeration and Redox

Aeration measurements were made using the platinum microelectrode method of Lemon and Erickson, and Redox measurements were made with the same electrode using a portable potentiometer.

RESULTS AND DISCUSSION

Mechanical Composition

The mechanical analysis of these soils indicates they are all sands. There is some variation in the amount and distribution of the sands between the various soil series, but there is also considerable variation between different samples taken from the same sampling area. Only the Granby soil on circle 47 had detectable amounts of clay, and then only 1% was present. The bulk of the sands were in the medium and fine sand range or from 100 to 500 microns diameter.

These soils have single grain structure except for the occasional Fe cemented ortstein horizons. With this exception, they should be durable to tillage and other manipulations. The only physical problem is of water retention or drouthiness.

Soil Water Characteristics, Bulk Density and Hydraulic Conductivity

These determinations were all made on the same core samples. Because there did not appear to be any trends in these values from successive samplings, all of the values were averaged and presented in table 36. When the eighty values (two sites sampled four times with ten samples per sampling) for each soil series are compared, they are remarkably similar.

All the A_p horizons hold more water and have a lower bulk density than the B or C horizons. The deeper horizons decrease in water retention with depth. There is some additional water held by the imperfectly drained AuGres and Roscommon that had more organic matter.

The 0.1 atmosphere moisture percentage might be considered the field capacity (water present in soil after free drainage) of these soils. Considering this value, the A_p of the Roscommon averaged 30% as compared to 19% for the Rubicon. The deeper horizons were quite variable from sample to sample, but the averages were quite similar, ranging from 10 to 16%, except for Rubicon C which was lower. If either of the Granby soil sites had had a mucky surface, as some of the Granby on the project does, the moisture characteristic would have been higher and the bulk density less.

The bulk densities of these sands were similar, although these values for the A_p were altered early in the season by tillage.

All of the average hydraulic conductivities were quite similar except

Table 36. SUMMARY OF AVERAGES OF SOIL PHYSICAL PROPERTIES BY SOIL SERIES AND HORIZONS

Soil Type	Horizon	Soil Water Characteristics ---- Tension - atm. ----				Bulk Density	Hydraulic Conductivity
		0.01	0.1	0.33	1.0		
		-Percent water by volume-				g/cc	cm/hr
Rubicon Sand	A_p	43	19	18	14	1.4	32
	B	38	10	9	8	1.6	54
	C	38	8	8	7	1.6	84
Granby	A_p	42	25	18	15	1.4	16
	B	38	16	10	8	1.6	33
	C	35	10	6	5	1.6	40
Roscommon	A_p	44	30	23	22	1.2	34
	B	35	16	10	8	1.6	28
	C	33	10	6	5	1.7	42
AuGres	A_p	44	25	20	18	1.2	38
	B	40	15	12	10	1.5	33
	C	34	11	7	6	1.6	38

for the Granby A_p which was about one-half the average and the Rubicon C which was twice the other values. All these values are high and confirm that these are very permeable soils.

Infiltration

The infiltration determinations are summarized in table 37 giving the values at each of the four samplings. The data is extremely variable, and no obvious trends are evident. Soil variability seems to be amplified by the infiltration measurement even though each value is an average of ten measurements for the surface and five for the subsurface. Much of the surface had just been cleared, and the sampling occurred as it was being brought under cultivation and irrigation. The subsoils in these sands are also very variable. Nevertheless, all of the values are extremely high; the lowest reading was about 10 cm per hour. There should be no problem with water application with infiltration rates of these soils as long as there is adequate underdrainage.

Oxygen Diffusion Rates and Redox Potential

Oxygen diffusion rates were determined after the heavy application of wastewater that occurs at the far end of a large irrigation rig. Even though the water stood on the surface in the lower places for fifteen to thirty minutes, the duration of oxygen deficient conditions, which occurred after visible infiltration from the surface ceased, persisted for less than thirty minutes. Under these rapidly changing conditions, plants would not be harmed by this stress. The redox potentials in the soil would not be reduced either.

Under several of the circles, where the drainage system has failed, flooding of the soil has developed. We were not aware of this as our field crew had completed their measurements before this developed. Under these conditions of drainage failure, oxygen deficiencies and redox change are to be expected and plant growth may be adversely affected. The solution of this problem is to bring the drainage system up to the original specifications.

ADDENDUM

Since this study was completed, small areas of Saugatuck and areas of slowly permeable AuGres soils have been observed in circle 26. These soils have not been studied. They are difficult to locate until after a period of irrigation reveals their location. Once these areas have been found, they should be mapped and studied to determine what sort of modification is necessary to overcome the flooding that is occurring on these soils.

Table 37. SUMMARY OF INFILTRATION RATES DETERMINED DURING 1973-1975.

Condition		Infiltration Rates											
		Initial Dry				Initial Wet				Minimun Wet			
Time *		1st	2nd	3rd	4th	1st	2nd	3rd	4th	1st	2nd	3rd	4th
Soil Type	Circle Number	cm/hr											
Rubicon													
Surface	3	82	79	47	90	51	68	36	42	51	64	48	35
	5	63	50	59	80	48	46	28	90	48	42	53	26
Granby													
Surface	46	26	44	49	48	12	30	23	22	9	39	14	19
	47	13	31	43	39	7	17	20	18	2	15	15	17
Subsurface	46	76	125	86	64	51	60	35	30	36	61	36	41
	47	73	14	45	93	34	6	19	50	29	4	57	19
Roscommon													
Surface	42	26	29	39	29	17	27	15	16	12	23	12	12
	48	58	49	48	23	38	31	27	11	25	29	8**	19
Subsurface	42	51	60	51	26	40	50	28	13	44	57	13	35
	48	40	32	19	35	33	21	11	27	26	17	22**	10
AuGres													
Surface	23	74	50	51	46	45	53	25	22	37	38	18	21
	40	23	29	40	67	15	15	16	36	18	15	38	17
Subsurface	23	39	31	65	53	49	39	44	26	34	37	30	44
	40	43	39	22	51	18	26	13	37	21	31	37	11

* Time of sampling was 1st in Spring 1973, 2nd in August 1973 before the application of wastewater, 3rd in summer 1974 after limited wastewater application and 4th in Summer 1975 after all the circles had a full year of application.

** Circle 48 was not accessible for the 3rd and 4th sampling so Circle 50 was substituted.

SECTION VII

MICROBIAL STUDIES

The principal objective of the work discussed in this section was to determine the type and quantity of microorganisms present on the Muskegon land treatment site, with particular reference to those involved in nitrogen transformations.

Microbial populations were determined on three soils representative of the soil diversity present at the Muskegon site. The populations were analyzed by the following methods: nitrifiers, MPN (most probable number), using an ammonium carbonate medium and testing for the appearance of NO_3; denitrifiers, MPN in NO_3 broth incubated anaerobically and tested for disappearance of both NO_3 and NO_2; aerobes, plate count on soil extract agar; anaerobes, MPN in NO_3 broth and observing turbidity.

The most striking result is the low numbers of nitrifiers on the Rubicon and AuGres soils at the start of irrigation (table 38). This is likely due to the low pH, 4.6 and 6.0, respectively, since acidic conditions are known to be unfavorable to chemolithotropic nitrifiers. The high NH_4^+ in the soil at the Rubicon site is also explained by this nitrification limitation. However, as wastewater was added, the pH increased, allowing proliferation of nitrifiers at the expense of NH_4^+, their energy source. The initial low pH of the Rubicon site was due to the forest cover. By comparison, the farmed Granby soil had a neutral pH, high nitrifier population, and low NH_4^+ at the onset of irrigation. It maintained this quasi-steady-state condition through the second year.

The denitrifier population increased slightly with irrigation, particularly in the Rubicon soil. The denitrifier population relative to total aerobes and anaerobes was quite low in all of these soils compared to most other agricultural soils. A possible explanation is the low organic matter and aerobic conditions of these very sandy soils.

The aerobic population was fairly stable through the irrigation. It was significantly higher in the Granby soil as expected because of its higher organic matter content.

The anaerobic populations showed a decrease with wastewater irrigation. A possible explanation is that sporeforming anaerobes, i.e., clostridia, may have been stimulated to germinate but did not survive under the aerobic conditions present.

In summary, it is clear that the irrigation had no detrimental effect on the soil microbial community, and, in the case of the nitrifiers, it stimulated their development, thus assuring the conversion of NH_4^+ to NO_3^- in the soil.

Table 38. CHANGE IN MICROBIAL POPULATIONS AND SELECTED CHEMICAL PARAMETERS IN RESPONSE TO INITIAL WASTEWATER IRRIGATION ON THREE SOIL TYPES.

		Microbial populations (nos·g dry wt^{-1})*			
Site	Date	Nitrifiers	Denitrifiers	Aerobes	Anaerobes
		(x10^1)	(x10^3)	(x10^4)	(x10^5)
5	6-11-74	2.3	8.4	3.6	75
(Rubicon)	8-05-74	470	48	4.4	22
	6-23-75	1600	46	1.2	2.6
	9-10-75	4200	170	15	13
24	6-11-74	13	22	120	98
(AuGres)	8-05-74	160	49	4.0	10
	6-23-75	2800	42	5.4	3.8
	9-10-75	1700	88	8.3	17
46	6-11-74	1900	46	18	55
(Granby)	8-05-75	420	36	10	23
	6-23-75	1400	320	9.4	22
	9-10-85	7000	110	12	11

* Samples were taken from the same site. Four replicate soil samples, each comprised of four subsamples, were taken from the same site.

Table 38. CHANGE IN MICROBIAL POPULATIONS AND SELECTED CHEMICAL PARAMETERS IN RESPONSE TO INITIAL WASTEWATER IRRIGATION ON THREE SOIL TYPES. (CONTINUED)

Water added (cumulative in.)	pH	NH_4-N (ppm)	NO_3-N (ppm)	Total C (%)	Site Listing
	4.6	40.8	2.3	2.0	Forest cleared in 1973
85.1	6.8	20.0	5.2	0.7	
107.7	6.0	3.4	9.6	1.0	
148.7	6.6	0.2	8.1	1.1	
	6.0	1.1	6.7	1.9	Abandoned farm land
71.2	7.0	7.8	1.1	1.5	
80.7	6.5	2.5	6.7	1.7	
113.6	6.2	0.2	9.5	2.8	
	7.3	0.6	7.0	2.2	Actively farmed
27.8	-	-	-	-	
33.0	5.7	2.2	58.2	4.4	
41.2	7.0	0.7	10.6	2.1	

SECTION VIII

PESTICIDES AND INDUSTRIAL TRACE ORGANICS

INTRODUCTION

It is to be expected that wastewaters from a large municipality will contain a wide spectrum of potentially toxic trace organics originating in industry, warehouse facilities, or distribution and trade channels. Also, in a newly established system, there is the probability that not all sources of storm flow have been identified and isolated from the wastewater collection network.

In the Muskegon and Whitehall systems, such storm flows can originate in areas of intensive vegetable production as well as in urban landscapes. Until non-point sources are identified and isolated or otherwise regulated, the sewage collection system can serve to channel pesticides in runoff and sediments from scattered areas of use to a common point--the wastewater treatment facility.

Data reported in this section represent a surveillance level monitoring of soils and waters associated with the two Muskegon County wastewater management systems. Four objectives were in view:

a) To obtain an inventory of readily detectable and potentially toxic pesticides and other trace organics in incoming raw sewage.

b) To derive preliminary information regarding the fate of trace organics at various stages of treatment.

c) To obtain a baseline inventory of trace organics in representative soils prior to irrigation with wastewater.

d) To observe changes in level and profile distribution that might provide an early indication of the extent to which recalcitrant compounds in wastewater may accumulate in soils and pose a long term residual threat to crop production and terrestrial wildlife or to contiguous aquatic environments and groundwater supplies.

Attention was focused on organic species which can be detected at very low concentrations by gas-liquid chromatography (GLC), using an electron capture detector (ECD). These include many of the persistent halogenated compounds of environmental concern.

Sampling of wastewaters was initiated with the first flow of raw sewage to the Muskegon Wastewater Management System in June 1973. Monthly composites of raw sewage from June through November 1973 were used to inventory chromatographic peaks, make tentative peak assignments and modify procedures for routine analysis. The first useful analyses of raw sewage were obtained in December 1973, at which time routine monthly analysis was initiated (monthly composites of twice-daily grab samples). Beginning in April 1974, daily grab samples were composited for monthly analysis of discharges (after aeration and settling) into the storage lagoons. At this time also, monthly compositing (daily grab samples) was begun at Mosquito Creek and Black Creek outfalls (SW-05 and SW-34, Fig. 1). After field irrigation began in May 1974, flows out of storage (before and after chlorination) were composited periodically. At Whitehall, routine monthly analysis of raw sewage and of treated discharges into storage was begun in April 1975 (monthly composites of weekly grab samples).

Eight special study sites, representing four soil types, were sampled twice before wastewater was applied and twice yearly since full scale irrigation was initiated in 1974. Additional analyses for background were performed on soils from 25 sites sampled in 1972 or 1973.

The special study sites at Muskegon (Fig. 1) were on AuGres sand (sites 03 and 04, circles 21 and 24), Granby sand (sites 08 and 26, circles 47 and 44), and Roscommon sand (sites 16 and 17, circles 41 and 42). Two sites at Whitehall (not shown in Fig. 1) were on Rubicon sand (sites 30 and 31, circles W-3 and W-1).

GLC peaks which correspond to those for 29 known reference chemicals have been encountered in soils or waters. The corresponding peak positions in output from two different GLC columns were monitored routinely for all extracts of soils and waters. Thin layer chromatography and, for certain chemicals, a third or fourth GLC column were also used for confirmation.

Three additional peaks were monitored routinely, beginning August 1975, but have not been identified with known compounds. These were frequently prominent in raw influent and in discharges to storage. They appeared at greatly attenuated levels in soils and in outfall waters.

PROCEDURES

Sampling methods and analytical procedures are described in detail in Appendix II. They are described briefly below.

Sampling and Extraction of Soils

Four cores were composited from depths of 0 - 15, 46 - 61, and 91 - 107 cm (0 - 6", 18 - 24", and 36 - 42")--the third depth was not sampled prior to 1975. Aliquots (100 g field moist soil) were deactivated with water and extracted with two successive 100 ml aliquots and a third 50 ml aliquot of 2:1 benzene-isopropanol. The isopropanol was removed with water. The benzene extract was dried by passing through anhydrous sodium sulfate and concentrated twice to a final volume of 10 ml.

Sampling and Extraction of Waters

Water samples were taken daily (or as noted in tables) and accumulated at 4° C over periods of 2 to 5 weeks. Raw influent and discharges into storage through 1975 were separated by centrifugation and filtering into aqueous and particulate phases. Particulate phases were extracted with 2:1 benzene-isopropanol as for soils. Water samples (1.5 liters) were extracted with 4 successive 50-ml aliquots of methylene chloride. The extract was concentrated to 5 ml and transferred into benzene (with successive concentration steps to remove methylene chloride). The final volume in benzene was 10 ml.

Cleanup of Extracts

Prior to analysis, benzene extracts were cleaned up and separated into groups of chemicals by fractional elution off from Florisil.

Detection and Quantitation of Organics

Detection and quantitation were by gas-liquid chromatography (GLC), using 1.5% OV-17/1.95% QF-1 on Gas Chrom Q in glass columns (3 mm I.D. x 1.83 m). Identification was by retention time confirmed on one or more additional columns and by thin layer chromatography (silica gel). A Beckman GC-5 was used, with a non-radioactive electron capture detector (helium arc discharge). Instrument parameters were optimized daily for maximum sensitivity. Integrator (Autolab System I) parameters were set to reject peaks with heights less than 3 times baseline noise.

An injection volume of 4 µl was used for samples. Reference standards were injected after every third sample, at volumes ranging from 1 to 6 µl to provide a standard curve. Standard concentrations of 1/10 X, 1 X, or 10 X were used to provide ranges of linear response appropriate for sample concentrations encountered.

Confirmation of Peak Identities

Chemicals as reported have been confirmed routinely on two columns (1.5% OV-17/1.95% QF-1 and 6% QF-1), and by thin layer chromatography (silica gel). For certain chemicals and extracts, 2% SE-30 or 3% DEGS columns have also been used for confirmation. (Table II-2, Appendix II).

TRACE ORGANICS IN WATERS

With the exception of diethylhexylphthalate (DEHP), chemicals reported for incoming wastewaters in this study are pesticides or isomers or metabolites of pesticides. Identification of sources was beyond the scope of the investigation. However, some consideration of probable sources and modes of entry for trace organics into wastewater flows at Muskegon and Whitehall will be helpful in evaluating the data.

Probable Sources and Modes of Entry

Sewage treated at Muskegon and Whitehall comes from 14 municipalities, with approximately 140,000 residents and 200 industries. Most of it (27 MGD in 1975) goes into the Muskegon system. Flows at Whitehall are about 1 MGD (Muskegon County Dept. of Public Works, 1975; USEPA, Region V, 1976).

Sixty percent of the flows at Muskegon come from industry, with the major contributor a paper manufacturer. A major contributor at Whitehall is a tannery. Manufacturers of chemicals include several companies that produce primary chemicals and intermediates, pesticides, plastics, resins, elastomers. Other industries that undoubtedly use organic chemicals of environmental concern are manufacturers of foundry products, heavy machinery, automotive engines, parts and accessories (Directory of Michigan Manufacturers, 1976).

Supporting these basic industries are warehousers and distributors serving local, state, national and international trade channels by rail and truck, as well as through the Port of Muskegon and the St. Lawrence Seaway. There are also numerous operators involved in various aspects of industrial waste disposal: waste haulers, waste takers and processors, barrel renderers, etc.

This complex of activities affords numerous opportunities for point source contamination due to accidents, inappropriate handling or storage, or inadequately controlled disposal or discharge.

"Truth in pollution" legislation (Act 200, Mich. P.A. 1970, and later amendments to Act 245, P.A. 1929) requires that industrial and commercial producers of wastewaters (other than sanitary sewage) file annual reports with the Michigan Water Resources Commission, listing critical materials and wastewater outfalls. A fee is assessed to cover costs of surveillance by the Commission.

Types of outfall registered by industries in the Muskegon and Whitehall areas include discharges into surface waters (directly or through storm sewers) and a variety of discharge methods that may lead ultimately to groundwater (lagoons or seepage ponds with no outlet, septic tanks and tile fields, overland flow). Large quantities of noxious liquid wastes and recoverable by-products are transported by licensed waste haulers to independent industrial waste processors operating locally, elsewhere in Michigan, or out of state. Sludges that accumulate in lagoons and seepage ponds have in the past been incinerated, buried in landfills, or abandoned in favor of new discharge sites.

Since the two county treatment systems became operational, state and local authorities have encouraged the diversion of compatible wastewaters from industry into sanitary sewers connected to the county systems. The major contributor to flows at the Muskegon site (the paper mill) initiated diversion in June 1973. The tannery at Whitehall connected up in late 1974. The number of connected discharges has increased over the period of this study. Diversions of 50 to 80% or more were registered by a number of companies in 1975. However, numerous industries and a number of smaller municipalities were either not connected or had diverted less than 50% of their wastewater into either system through 1975 (Michigan Water Resources Commission, Surveillance Fee Listings, 1973, 1974, 1975).

Increasing numbers and diversity of source discharges may have contributed to changes in spectrum of trace organics encountered in this study. It is likely that wastewaters will become increasingly complex and variable in composition as more of the existing discharges from industry and from suburban residential and commercial areas are connected to the system and as new industries, attracted by the county's wastewater treatment capabilities, move into the area.

A wide range of chemicals is used or produced in large volume. The bulk of these are identified in critical materials registrations only by broad categories (chlorinated benzenes, nitrobenzenes, aromatic amines, etc.). The probable range of organic species which may appear in wastewaters is augmented by unknown or unlisted by-products of manufacturing or of pretreatment before discharge. Discharges can vary widely from time to time with production schedules that may involve a succession of weekly campaigns for production of two or more intermediates leading to a major product. Wastewaters from paper manufacturing are extremely complex and vary with pulping method, pulp species, and with treatment given to pulping effluents before discharge (Hrutfiord et al., 1975).

Numerous instances of contamination of surface and groundwaters associated with chemical industries in the Muskegon and Whitehall areas have occurred (Muskegon Chronicle, December 12, 1975; Detroit Free Press, December 29, 1976 and April 12, 1977). The Michigan Water Resources Commission has determined that contaminated groundwaters shall be purged by pumping into the county wastewater treatment systems. It is unlikely that much of this was done during the period of this study, however.

At the present state of the art, both dischargers and control agencies are handicapped by uncertainties regarding parameters which should be monitored and by analytical difficulties in resolving complex mixtures and positively identifying individual organic species.

The lack of positive identification by other than chromatographic parameters seriously limits the credibility of chemical assignments given in this report. Phthalates are listed as critical materials by a number of companies, supporting the identification here of DEHP. Of the pesticides, only phorate (Thimet^R) is known to have been produced in the Muskegon area where it was identified frequently in wastewaters in 1975. However, it appears that major production may not have been undertaken until early 1976.

Circumstantial support for several pesticides is to be found in known patterns of use and in known sales for "restricted use" pesticides which must be reported by licensed dealers (Michigan Department of Agriculture, Regulation No. 633, 1972). There is good reason to expect that pesticides in current use or persistent residues from past use will enter wastewater flows, directly or indirectly, from hydrologic systems that converge in the Muskegon and Whitehall areas.

Major industrial dischargers in the Muskegon area take their feedwaters from Muskegon Lake, Mona Lake or streams that flow into them, or from contiguous groundwaters. Sixty percent of the annual wastewater flow at the Muskegon treatment site comes from the paper mill, which takes essentially all of its processing water from Muskegon Lake. Contaminants in Muskegon Lake may well appear at the treatment site at levels reduced by less than fifty percent. Much greater dilution would be expected for contaminants from Mona Lake or other lesser sources of feedwater.

Pesticides and other pollutants in these lakes can originate locally in storm flows from residential, commercial and industrial areas. Chronic contamination of surface and groundwaters by discharges from chemical industries has occurred along streams entering both lakes. Both receive drainage from watersheds extending northeasterly, hence normally downwind. Thus, airborne pollutants generated locally can be intercepted and returned. Vegetables, mainly celery, are grown in drained lowlands just east of both lakes. Floodwaters of the Muskegon River occasionally wash across the diked fields near its mouth.

Water and sediments entering Muskegon and Mona Lakes can also carry contaminants from point and non-point sources scattered widely over extensive river basin areas. The Muskegon River basin is one of the largest in Michigan (2660 mi^2, or 6890 km^2). Fifty percent of the area is forested and includes a large proportion in recreational areas and concentrated resort development; 25% is in agriculture, including important areas of cash crop and intensive vegetable production. Over 20 industries and 9 municipalities use the surface waters of the river for wastewater assimilation (Great Lakes Basin Commission, 1976; Wright, 1974; see also National Cooperative Soil Surveys for Counties of Muskegon, Newaygo, Mecosta and Osceola).

The Black Creek watershed lies almost entirely in Muskegon County. There are areas of agricultural production in the eastern half of the basin including vegetables and cash crops on organic soils just east of the wastewater irrigation site. A large chemical plant is located in a thinly populated marginal area along the middle reaches of the stream. The lower half of the basin becomes increasingly urbanized on approach to Mona Lake, but there are scattered farms, including areas near the lake, that are managed intensively for celery and other vegetables.

A number of pesticides implicated in this study were currently and widely used for insect control in agriculture and forestry and for landscaping and other uses in urban, suburban, resort and recreational areas. These, and persistent chemicals like DDT and endrin that were used extensively prior to the 1970's, can appear in substantial concentrations in streams during periods of heightened or turbulent flow resulting from runoff and erosion (Miles, 1976; Snow, 1977; Truhlar and Reed, 1976).

Soluble materials and pesticide-enriched fine sediments carried by streams can be widely dispersed in receiving lakes. Heavier bottom wash sediments are also enriched with pesticide residues. Deposition of sediments in flooding lowlands and in quiescent waters near the mouths of streams is a concentrating mechanism. The presence of such deposits increases the probability that persistent chemicals will be found in associated surface waters (Glooschenko, 1976). Flooding lowlands are often important groundwater recharge areas. Deposition of enriched sediments in these areas also increases the potential for contamination of groundwaters (Garrett et al., 1976).

Thus, there is good reason to expect that pesticides and other contaminants from basin-wide sources will appear in feedwaters used by industry. At times the concentrations may be substantial, and little change will occur between points of intake and discharge where water is used for cooling or for large volume processes compatible with low-grade water. This would be the primary mode of entry into flows received at the treatment site. System failures can occur, as when a malfunctioning sluice gate allowed high waters in Muskegon Lake to flow directly into municipal sewerage for periods during this study. Flows measured in the system indicate that infiltration of sewers occurs also in low-lying areas during periods when the watertable is high and that there are places in the system where storm sewers and sanitary sewers are still interconnected. Unusual flows associated with storm events or high water are, however, small when compared to base flow or to industrial flows that are known to originate in feedwaters taken from lakes or streams.

Some of the circumstances described above for the Muskegon system undoubtedly exist also at Whitehall. Celery is grown in lowlands near the mouth of White River and along its lower tributaries in Muskegon County. The basin includes important areas of vegetable production and general farming in Oceana and Newaygo Counties (Wright, 1974; also see National Cooperative Soil Surveys for these counties). Some of the fruit areas in Oceana County drain to White River. There are scattered resort developments and recreational areas in the basin and several small communities along the river.

The White River discharges into White Lake which opens on Lake Michigan. White Lake also receives discharges and storm flows from a concentration of industry around the lake as well as runoff from residential, commercial and resort areas. Well over 90% of the wastewater volume registered in 1975 for industrial outfalls in the Whitehall-Montague area was surface discharged and came mainly from a basic producer of chlorinated hydrocarbons. The plant is not connected to the Whitehall wastewater system; however, chemicals discharged to the lake or airborne and intercepted on downwind landscapes might well appear in feedwaters of other industries which do discharge into the Whitehall system.

To monitor the full range of chemicals known or suspected of being input at either the Muskegon or Whitehall treatment sites is beyond available funding and probably beyond presently available methodology. Analytical difficulties are complicated further by the likelihood that individual source chemicals are variously altered in diverse environments along pathways of local and regional circulation before coming together at the treatment sites. Fluctuations in volume and composition of flows from individual point or nonpoint sources make sampling to estimate loadings at a confluence point difficult if not impossible (Lake Michigan Interstate Pesticides Committee, 1972).

Only electron capturing species were monitored in this study. Electron capture was used for detection and quantitation because of its sensitivity for a number of chlorinated hydrocarbons that are known to be widely distributed and most likely encountered. DDT, dieldrin and PCB's are of particular concern in the Great Lakes Basin because of their known impact on fish and waterfowl and their persistence in soils and sediments (International Joint Commission, 1976; Schacht, 1972). These and other refractory organics can be useful for tracing pathways of circulation through the environment (Arthur et al., 1977; Miles, 1976; Roan, 1975; Snow, 1977). A broad spectrum of organics which might be expected from industry would not have been detected (Garrett et al., 1976).

Chemicals reported here were identified by chromatographic methods and confirmed on three or more media. Nevertheless, identities are presumptive rather than specific. The chromatographic parameters (Appendix II) are reproducible. The methods used and the data themselves are compatible with a large volume of data accessible in STORET (Merkle and Bovey, 1974) and with historical documentation categorized by geographical location, water types, sources, etc. in such compilations of available data as DAM (Hall et al., 1976) and Water DROP (Shackleford and Keith, 1976).

Raw Influent and Discharges into Storage

Because of the large number of probable sources and fluctuating flows from each, the composition of incoming wastewater can vary greatly over short periods of time. Chemicals entering sporadically may not be detected in grab samples taken at a given station. Some GLC peaks which were not found in raw influent did appear during the same compositing period in discharges into storage lagoons. Peaks for most chemicals did not decline in frequency or indicated range of concentration during aeration and settling. For these reasons, data for raw influent and for discharges into storage are best considered together for purposes of characterizing incoming wastewaters. Data for monthly composites are given in Tables 39 to 43. Frequencies and ranges of occurrence are summarized for 1974 and 1975 in Tables 47 and 48.

Industrial organics --

Diethylhexylphthalate (DEHP) was the only industrial organic identified in this study. Phthalates, as a class, have appeared on lists of critical materials from local industries. DEHP was found frequently at Muskegon at concentrations of 10^3 to 10^6 ng/l (Tables 39 to 42). An important source would have been from manufacture of paper products. It appeared at Whitehall in late 1974 at about the time the leather company reported its hook-up to the system (Table 43).

Numerous unknown peaks were not monitored. Beginning in August 1975, three unknown peaks that were frequently observed and often prominent were integrated, and their percentage contribution to total integrated peak area was recorded. These were at 115-118 sec, 164-168 sec and 247 to 253 sec on 1.5% OV-17/1.95% QF-1 (Rt ratios relative to aldrin = 0.9, 1.27 and 1.92). The first two peaks were not close to any major peak for any of the common Arochlors examined (1242, 1248, 1254, 1260). The third corresponded closely

Table 39. TRACE ORGANICS IN RAW INFLUENT, MUSKEGON, DECEMBER 1973 TO DECEMBER 1974.‡

Month	Compositing Period (twice daily grab samples)	p,p'-DDE	Endrin	Heptachlor	Heptachlor epoxide	1-hydroxy-Chlordene	α-BHC	Lindane	Diazinon	Phorate	2, 4-D (ME)	Vegadex (CDEC)	DEHP
		ng/l											
Dec	12-1-73 to 12-21-73	nd*	nd	nd	nd	nd	nd	89	nd	nd	nd	nd	$75x10^3$
Dec-Jan	17-22-73 to 1-21-74	nd	nd	nd	nd	nd	nd	140	nd	nd	nd	nd	$109x10^3$
Feb	2-1 to 2-27-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	$63x10^3$
Mar	2-28 to 3-19-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	$20x10^3$
Mar	3-20 to 4-4-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	$91x10^3$
Apr	4-8 to 4-30-74	324	nd	123	106	225	nd	nd	nd	nd	nd	323	$358x10^3$
May	5-1 to 5-14-74	35	10 †	363	2 †	nd	193	323	nd	nd	nd	nd	$650x10^3$
May	5-15 to 5-31-74	nd	nd	464	nd	270	nd	57	nd	nd	nd	nd	$172x10^3$
Jun-Jul	6-1 to 7-11-74	nd	nd	nd	nd	nd	nd	79	nd	nd	nd	nd	$21x10^3$
Jul	7-12 to 7-31-74	nd	nd	22	7	10†	340	97	nd	nd	nd	nd	$36x10^3$
Aug	7-31 to 8-29-74	nd	nd	nd	nd	nd	nd	268	nd	nd	$1.2x10^3$	nd	nd
Sep	8-30 to 9-30-74	nd	nd	nd	nd	nd	nd	100	nd	nd	nd	nd	nd
Oct	10-1 to 10-29-74	nd	nd	nd	nd	nd	nd	6	404	nd	nd	nd	$199x10^3$
Nov	10-30 to 12-1-74	nd	nd	nd	3 †	nd	nd	nd	nd	nd	nd	nd	$175x10^3$
Dec-Jan	12-2-74 to 1-10-74	nd	nd	nd	nd	nd	nd	5 †	nd	$6.3x10^3$	nd	nd	nd
Detected means (ng/l)		180	10	243	30	168	266	116	404	$6.3x10^3$	$1.2x10^3$	323	$164x10^3$

*nd = not detected

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 40. TRACE ORGANICS IN RAW INFLUENT, MUSKEGON, JAN TO DEC 1975.‡

Month	Compositing period (twice daily grab samples)	Aldrin	Dieldrin	p,p'-DDT	Heptachlor	Heptachlor epoxide	α-BHC	Lindane	Diazinon	Dimethoate	Phorate	Lasso	2,4-D (ME)	2,4-D (BE) I	2,4-D (BE)II	2,4-D (IPE)	DEHP
		ng/l															
Jan	1-6 to 1-31-75	nd*	nd	28	nd	nd	nd	31	nd	347	nd	nd	nd	nd	nd	nd	2,620x10^3
Feb	2-4 to 2-28-75	4†	nd	nd	nd	194	nd	374	nd	nd	3.5x10^3	nd	nd	nd	nd	nd	nd
Mar	3-4 to 3-31-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.1x10^3	nd
Apr	4-1 to 4-30-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	630	nd	nd	nd
May	5-2 to 6-2-75	nd	nd	nd	nd	nd	nd	102	nd	nd	2.x10^3	nd	nd	nd	nd	nd	677x10^3
Jun	6-2 to 7-2-75	nd	nd	nd	nd	nd	34	20	nd	nd	32.x10^3	nd	nd	nd	nd	nd	53x10^3
Jul	7-2 to 7-30-75	nd	nd	nd	8	nd	nd	30	nd	nd	nd	nd	4.x10^3	nd	nd	nd	60x10^3
Aug	8-2 to 9-2-75	nd	tr**†	nd	nd	nd	nd	611	1.5x10^3	nd	9,x10^3	200	1.x10^3	nd	nd	nd	55x10^3
Sep	9-2 to 10-2-75	nd	nd	nd	nd	nd	nd	20	nd	nd	6.6x10^3	9.3x10^3	nd	nd	200	nd	nd
Oct	10-2 to 11-4-75	nd	nd	nd	nd	nd	517	815	nd	nd	7.5x10^3	nd	nd	nd	nd	nd	1,067x10^3
Nov	11-4 to 11-28-75	nd	nd	nd	90	21	96	575	nd	833	88.x10^3	nd	nd	nd	nd	nd	50x10^3
Dec	12-2-75 to 1-2-76	nd	nd	nd	nd	nd	nd	83	nd	3.2x10^3	nd	200	5.5x10^3	nd	nd	500	193x10^3
Detected means (ng/l)		4	tr	28	49	108	216	266	1.5x10^3	1.5x10^3	21.x10^3	3.2x10^3	3.5x10^3	630	200	800	597x10^3

*nd = not detected

**tr = Trace

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 41. TRACE ORGANICS IN DISCHARGES INTO STORAGE LAGOONS, MUSKEGON, APRIL TO DEC. 1974.‡

Month	Compositing period (daily grab samples)	Dieldrin	p,p' - DDE	Heptachlor	Heptachlor epoxide	1-hydroxy-chlordane	α-BHC	Lindane	δ-BHC	Methyl parathion	Lasso	Vegadex	DEHP
		ng/1											
April	4-8 to 4-30-74	nd*	244	nd	nd	341	nd	224	nd	nd	nd	nd	419x10^3
May	5-1 to 5-14-74	nd	345	199	nd	nd	nd	155	nd	nd	nd	nd	348x10^3
May	5-15 to 5-31-74	nd	nd	nd	nd	144	18	92	nd	nd	nd	nd	269x10^3
Jun-Jul	6-1 to 7-11-74	nd	nd	nd	nd	187	51	73	nd	nd	nd	nd	67x10^3
Jul	7-12 to 7-31-74	nd	nd	37	80	512	40	151	nd	nd	nd	10	60x10^3
Aug	7-31 to 8-29-74	16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sep	8-30 to 9-30-74	nd	nd	nd	nd	25	nd	nd	127	38†	12.8x10^3	nd	1,233x10^3
Oct	No sample	---	---	---	---	---	---	---	---	---	---	---	---
Nov.	No sample	---	---	---	---	---	---	---	---	---	---	---	---
Dec-Jan	12-2-74 to 1-10-75	nd	nd	nd	nd	255	nd	151	nd	nd	nd	nd	nd
Detected means (ng/1)		16	294	118	80	244	36	141	127	38	12.8x10^3	10	216x10^3

*nd = not detected

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 42. TRACE ORGANICS IN DISCHARGES INTO STORAGE LAGOONS, MUSKEGON, JAN. TO DEC. 1975. ‡

Month	Compositing period (daily grab samples)	Aldrin	Endrin	o,p-DDD	o,p-DDE	p,p'-DDE	Heptachlor	Heptachlor epoxide	1-hydroxy-chlordene	α-BHC	Lindane	Diazinon	Dimethoate	Phorate	Lasso	2,4-D(IPE)	DEHP
		ng/l															
Jan	1-6 to 1-31-75	nd	35	nd	nd	nd	nd	nd	nd	nd	56	3.8x10^3	290	nd	nd	nd	332.10^3
Feb	2-4 to 2-28-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	111	nd	nd	nd	nd	nd	289x10^3
Mar	3-4 to 3-31-75	26	nd	nd	3†	nd	nd	nd	nd	nd	9	nd	nd	nd	nd	nd	nd
Apr	4-1 to 4-30-75	nd	nd	nd	11	nd	nd	nd	nd	nd	nd	910	nd	nd	nd	nd	106x10^3
May	5-2 to 6-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd	nd	nd	260	nd	nd
Jun	6-2 to 7-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	3†	nd	nd	nd	nd	nd	nd
Jul	7-2 to 7-30-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	56†	nd	nd	2.x10^3	nd	nd
Aug	8-2 to 9-2-75	nd	nd	tr**†	nd	nd	nd	nd	nd	nd	84	nd	nd	3.3x10^3	1.4x10^3	nd	183x10^3
Sep	9-2 to 10-2-75	nd	nd	nd	nd	18	nd	nd	7†	nd	58	nd	nd	nd	10†	nd	167x10^3
Oct	10-2 to 11-4-75	nd	nd	nd	nd	nd	955	nd	nd	nd	729	nd	nd	nd	nd	nd	350x10^3
Nov	11-4 to 11-28-75	nd	nd	nd	nd	nd	nd	nd	2†	98	463	nd	nd	31.x10^3	1.3x10^3	1.6x10^3	2,017x10^3
Dec	12-2-75 to 1-2-76	nd	nd	nd	nd	nd	7	18	2†	nd	168	nd	1.7x10^3	2.4x10^3	nd	nd	142x10^3
Detected means (ng/l)		26	35	tr	7	18	481	18	4	98	168	1.6x10^3	995	12.x10^3	994	1.6x10^3	448.x10^3

*nd = not detected

**tr = Trace

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 43. TRACE ORGANICS IN RAW INFLUENT AND IN DISCHARGE INTO STORAGE, WHITEHALL, APR. TO DEC. 1975. ‡

Month	Compositing Period (Random grab samples)	Aldrin	p,p' - DDD	Heptachlor epoxide	1-hydroxy-chlordene	α-BHC	Lindane	Dimethoate	Lasso	2,4-D (ME)	2,4-D (BE)II	2,4-D (IPE)	DEHP	Heptachlor metabolites	Lindane plus isomers
		ng/l													
RAW INFLUENT															
Apr	4-1 to 4-30-75	nd*	nd	9	nd	nd	nd	770	nd	nd	nd	$5.x10^3$	nd	9	nd
May	5-2 to 6-2-75	nd	nd	nd	nd	nd	22	nd	nd	nd	nd	nd	nd	nd	22
Jun	6-2 to 7-2-75	nd	nd	nd	nd	nd	51	nd	nd	nd	9†	nd	nd	nd	51
Jul	7-2 to 7-30-75	nd	nd	nd	nd	nd	14	nd	nd	nd	nd	962	nd	nd	14
Aug	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Sep	9-2 to 10-2-75	8	nd	nd	nd	nd	97	nd	nd	nd	nd	nd	nd	nd	97
Oct	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Nov	11-4 to 11-28-75	nd	nd	nd	nd	nd	113	nd	nd	300	nd	500	nd	nd	113
Dec	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---
DISCHARGE INTO STORAGE															
Apr	4-1 to 4-30-75	nd	404	26	nd	404	nd	$2.5x10^3$	nd	nd	nd	$1.4x10^3$	nd	26	404
May	5-2 to 6-2-75	nd	nd	nd	3†	nd	3†	nd	312	nd	nd	nd	nd	3†	3†
Jun	6-2 to 7-2-75	10	nd	nd	nd	nd	47	nd	nd	nd	nd	nd	nd	nd	nd
Jul	7-2 to 7-30-75	nd	nd	nd	nd	nd	25	nd	nd	nd	nd	nd	nd	nd	25
Aug	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Sep	9-2 to 10-2-75	nd	nd	nd	nd	nd	137	nd	nd	nd	nd	210	$2.x10^3$†	nd	137
Oct	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Nov	11-4 to 11-28-75	nd	nd	nd	nd	nd	nd	nd	nd	$4.2x10^3$	nd	$6.x10^3$	$5.x10^3$†	nd	nd
Dec	No sample	---	---	---	---	---	---	---	---	---	---	---	---	---	---

*nd = not detected

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 44. TRACE ORGANICS IN PRE-CHLORINATION FLOWS AND IRRIGATION WATER, MUSKEGON, JUNE 1974 TO DEC. 1974. ‡

Month	Compositing period (Random grab samples)	Dieldrin	p, p' - DDE	1-hydroxy-chlordene	α-BHC	β-BHC	Lindane	Lasso	DEHP	Total DDT species
		ng/1								
Prechlorination flows (out of storage lagoons)										
Jun-Jul	6-1 to 7-11-74	nd*	3†	57	nd	nd	36	315	$19x10^3$	3
Jul	7-12 to 7-31-74	nd	3†	nd	nd	nd	nd	nd	nd	3
Aug	7-31 to 8-29-74	nd	nd	nd	nd	nd	95	nd	nd	nd
Oct	10-1 to 10-29-74	nd	nd	62	nd	nd	32	nd	nd	nd
Nov	10-30 to 12-1-74	nd	nd	nd	nd	133	nd	nd	nd	nd
Dec	No sample	---	---	---	---	---	---	---	---	---
Irrigation waters (pumps #1 and #2)										
Jul #1	7-12 to 7-31-74	nd	nd	nd	nd	nd	371	nd	$112x10^3$	nd
#2	7-12 to 7-31-74	nd	nd	nd	nd	nd	nd	nd	$53x10^3$	nd
Aug #1	8-12 to 8-31-74	nd	nd	nd	nd	nd	nd	nd	nd	nd
#2	8-12 to 8-31-74	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sep #1	9-12 to 9-31-74	146	nd	nd	nd	nd	nd	nd	$32x10^3$	nd
Oct	No sample	---	---	---	---	---	---	---	-----	---
Nov #1		nd	nd	nd	43	nd	41	nd	nd	nd
#2		nd	nd	nd	143	nd	42	nd	nd	nd
Dec	No sample	---	---	---	---	---	---	---	-----	---
Detected means (ng/1)		146	3	60	69	133	93	315	$54x10^3$	3

*nd = not detected
†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 45. TRACE ORGANICS IN NORTH OUTFALL WATERS (SW-05, MOSQUITO CREEK), MUSKEGON; APR 74 TO DEC 75. ‡

Month	Compositing period (daily grab samples)	Aldrin	Dieldrin	p,p' - DDE	Heptachlor	Heptachlor epoxide	1-hydroxy chlordene	α-BHC	β-BHC	Lindane	Diazinon	Atrazine	Lasso	2,4-D(BE)II	Vegadex	DEHP
		ng/1														
Apr	4-8 to 4-30-74	nd*	nd	7†	nd	nd	nd	nd	nd	nd	nd	nd	298	nd	nd	nd
May	5-1 to 5-14-74	nd	nd	8†	nd	nd	nd	nd	nd	nd	nd	nd	119†	nd	nd	nd
May	5-15 to 5-31-74	nd	nd	8†	nd	nd	nd	25	nd	nd	nd	nd	183	nd	nd	15x10^3
Jun-Jul	6-1 to 7-11-74	14	nd	6†	5†	nd	nd	nd	nd	11	nd	nd	415	nd	32	10x10^3
Jul	7-12 to 7-31-74	nd	31	6†	47	25	145	53	nd	37	nd	nd	625	203	136	3x10^3†
Aug	7-31 to 8-29-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sep	8-30 to 9-30-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	48†	292x10^3	nd	nd	nd	nd
Oct	10-1 to 10-29-74	nd	nd	nd	nd	nd	nd	nd	46	84	521	nd	100†	nd	nd	nd
Nov.	10-30 to 12-1-74	nd	nd	nd	nd	nd	nd	112	nd	375	483	nd	nd	nd	nd	nd
Dec-Jan	12-2-74 to 1-6-75	nd	nd	nd	nd	nd	nd	11†	nd	nd	nd	nd	350	nd	nd	nd
Jan	1-6 to 1-31-75	nd	nd	nd	nd	nd	nd	nd	nd	5†	nd	nd	nd	nd	nd	nd
Feb	2-4 to 2-28-75	nd	nd	nd	nd	nd	nd	4†	nd	2†	nd	nd	nd	nd	nd	nd
Mar	3-4 to 3-31-75	nd	nd	nd	nd	nd	nd	19	nd	178	nd	nd	nd	nd	nd	nd
Apr	4-1 to 4-30-75	nd	nd	nd	nd	nd	nd	nd	nd	150	nd	nd	nd	650	nd	nd
May	5-2 to 6-2-75	4†	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	359	195	nd	nd
Jun	6-2 to 7-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	33†	nd	nd	nd
Jul	7-2 to 7-30-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	18†	nd	nd	nd
Aug	8-2 to 9-3-75	nd	nd	nd	nd	nd	nd	1†	nd	1†	nd	nd	nd	nd	nd	nd
Sep	9-2 to 10-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	115x10^3
Oct	10-2 to 11-4-75	nd	nd	nd	5†	nd	nd	nd	nd	2†	nd	nd	nd	nd	nd	nd
Nov	11-4 to 11-28-75	nd	nd	nd	nd	1†	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dec	12-2-75 to 1-2-76	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	25†	nd	nd	10x10^3
Detected means (ng/1)		9	31	7	19	13	145	37	46	84	334	292x10^3	226	349	84	31.x10^3

*nd = not detected

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 46. TRACE ORGANICS IN SOUTH OUTFALL WATERS (SW-34, BLACK CREEK), MUSKEGON, APR 74 TO DEC 75.‡

Month	Compositing period (daily grab samples)	Aldrin	p,p'-DDE	Heptachlor	Heptachlor epoxide	α-BHC	Lindane	δ-BHC	Diazinon	Phorate	Lasso	2,4-D(BE)I	2,4-D(BE)II	2,4-D(IPE)	Vegadex	DEHP
		ng/l														
Apr	4-8 to 4-30-74	nd*	nd	nd	nd	nd	nd	nd	nd	nd	141	nd	nd	nd	nd	nd
May	5-1 to 5-14-74	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
May	5-15 to 5-31-74	nd	5†	1†	nd	nd	39	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jun-Jul	6-1 to 7-11-74	22	2†	9	nd	nd	10	nd	207†	nd	nd	69	nd	nd	8	2.8x10^3†
Jul	7-12 to 7-31-74	39	nd	nd	nd	nd	3†	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aug	7-31 to 8-29-74	nd	nd	nd	nd	nd	42	nd	nd	nd	200	nd	nd	nd	nd	nd
Sep	8-30 to 9-30-74	nd	nd	nd	nd	16	12	7	nd	nd	nd	nd	nd	nd	nd	nd
Oct	10-1 to 10-29-74	nd	nd	nd	nd	nd	8	nd	nd	nd	100†	nd	nd	nd	nd	nd
Nov	10-30 to 12-1-74	nd	nd	nd	nd	nd	2†	nd	nd	nd	nd	nd	nd	nd	nd	nd
Dec-Jan	12-2-74 to 1-6-75	nd	nd	nd	nd	13	15	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jan	1-6 to 1-31-75	nd	nd	nd	6	nd	11	nd	nd	nd	nd	nd	nd	nd	nd	nd
Feb	2-4 to 2-28-75	nd	nd	nd	nd	nd	137	nd	nd	nd	nd	nd	nd	nd	nd	nd
Mar	3-4 to 3-31-75	nd	nd	nd	nd	nd	2†	nd	nd	63†	nd	nd	nd	nd	nd	nd
Apr	4-1 to 4-30-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
May	5-2 to 6-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	7.x10^3	nd	nd	nd	nd	nd
Jun	6-2 to 7-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Jul	7-2 to 7-30-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Aug	8-2 to 9-2-75	nd	nd	nd	nd	nd	1†	nd	nd	nd	nd	nd	nd	40†	nd	nd
Sep	9-2 to 10-2-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	32†	nd	nd	nd	nd	nd
Oct	10-2 to 11-4-75	nd	nd	nd	nd	nd	1†	nd	nd	nd	nd	nd	nd	nd	nd	nd
Nov	11-4 to 11-28-75	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	40.x10^3
Dec	12-2-75 to 1-2-76	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	217	nd	nd	nd
Detected means (ng/l)		30	4	5	6	14	22	7	207	63	1.5x10^3	69	217	40	8	21.x10^3

*nd = not detected

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 47. FREQUENCIES OF OCCURRENCE, TRACE ORGANICS IN WATERS, MUSKEGON, DEC 73 TO DEC 75.[‡]

Chemical	Raw sewage		After aeration and settling		After storage[#]	Mosquito Creek		Black Creek	
	Dec 73 to Dec 74	Jan 75 to Dec 75	Apr 74 to Dec 74	Jan 75 to Dec 75	Jun 74 to Dec 74	Apr 74 to Dec 74	Jan 25 to Dec 75	Apr 74 to Dec 74	Jan 75 to Dec 75
Total samples	15	12	8	12	13	10	12	10	12
					Occurrences[†]				
Aldrin	nd[*]	1	nd	1	nd	1	1	2	nd
Dieldrin	nd	1	1	nd	1	1	nd	nd	nd
Endrin	1	nd	nd	1	nd	nd	nd	nd	nd
DDT species	2	1	2	4	2	5	nd	2	nd
Heptachlor and/or metabolites	5	3	7	4	2	2	2	2	1
Lindane and/or isomers	10	10	7	10	7	6	6	8	5
Diazinon	1	1	nd	3	nd	3	nd	1	nd
Dimethoate	nd	3	nd	2	nd	nd	nd	nd	nd
Parathion (methyl)	nd	nd	1	nd	nd	nd	nd	nd	nd
Phorate	1	7	nd	3	nd	nd	nd	nd	1
Atrazine	nd	nd	nd	nd	nd	1	nd	nd	nd
2,4-D species	1	6	nd	1	nd	1	2	1	2
Lasso	nd	3	1	5	1	7	4	3	2
Vegadex	1	nd	1	nd	nd	2	nd	nd	1
DEHP	12	8	6	8	4	3	2	1	1

[#] Prechlorination flows (6 samples) and irrigation pump feed waters (7 samples).

[*] nd = not detected.

[†] Number of samples in which chemical was detected.

[‡] GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 48. DETECTED RANGES OF CONCENTRATION, TRACE ORGANICS IN WATER, MUSKEGON, DEC 73 TO DEC 75.‡

Chemical		Raw sewage Dec 73 to Dec 74	Raw sewage Jan 75 to Dec 75	After aerating and settling Apr 74 to Dec 74	After aerating and settling Jan 75 to Dec 75	After Storage# Jun 74 to Dec 74	Mosquito Creek Apr 74 to Dec 74	Mosquito Creek Jan 75 to Dec 75	Black Creek Apr 74 to Dec 74	Black Creek Jan 75 to Dec 75
		ng/l								
Aldrin	min	nd *	4†	nd	26	nd	14	4†	22	nd
	max								39	
Dieldrin	min	nd	tr†	16	nd	146	31	nd	nd	nd
	max									
Endrin	min	10†	nd	nd	35	nd	nd	nd	nd	nd
	max									
DDT	min	35	28	244	tr	3†	6†	nd	2†	nd
	max	324		345	18	3†	8†		5†	
Heptachor & metabolites	min	3†	8	25	2†	57	5†	1†	1†	6
	max	734	194	629	955	62	217	5†	9	
Lindane + isomers	min	5†	20	110	tr	32	11	1†	2†	1†
	max	516	$1.3x10^3$	224	729	371	487	197	42	137
Diazinon	min	404	$1.5x10^3$	nd	56†	nd	48†	nd	207†	nd
	max				$3.8x10^3$		521			
Dimethoate	min	nd	347	nd	290	nd	nd	nd	nd	nd
	max		$3.2x10^3$		$1.7x10^3$					

(continued)

Table 48. (continued)

Chemical		Raw Sewage		After aerating and settling		After Storage#	Mosquito Creek		Black Creek	
		Dec 73 to Dec 74	Jan 75 to Dec 75	Apr 74 to Dec 74	Jan 75 to Dec 75	Jun 74 to Dec 74	Apr 74 to Dec 74	Jan 75 to Dec 75	Apr 74 to Dec 74	Jan 75 to Dec 75
Parathion (methyl)	min max	nd	nd	38†	nd	nd	nd	nd	nd	nd
Phorate	min max	$6.3x10^3$	$2.x10^3$ $88.x10^3$	nd	$2.4x10^3$ $31.x10^3$	nd	nd	nd	nd	63†
Atrazine	min max	nd	nd	nd	nd	nd	$292x10^3$	nd	nd	nd
2,4-D species	min max	$1.2x10^3$	200 $6.x10^3$	nd	1.6x10	nd	203	195 650	69	40† 217
Lasso	min max	nd	200 $9.3x10^3$	$12.8x10^3$	10† $2.x10^3$	315	100† 625	18† 359	100† 200	32† $7.x10^3$
Vegadex	min max	323	nd	10	nd	nd	32 136	nd	8†	nd
DEHP	min max	$20.x10^3$ $650.x10^3$	$50.x10^3$ $2.6x10^6$	$60.x10^3$ $1.2x10^6$	$106.x10^3$ $2.x10^6$	$19.x10^3$ $112x10^3$	$3.x10^3$† $15.x10^3$	$10.x10^3$ $115.x10^3$	$2.8x10^3$†	$40.x10^3$

#Prechlorination flows (6 samples) and irrigation pump feed waters (7 samples).

*nd = not detected.

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

†Below usual range of confident quantitation (Appendix II, Table 2).

to a major peak in Arochlors 1254 and 1260.

The third peak (247-253 sec) appeared in the first (petroleum ether) eluant from Florisil, as did the reference Alachlors. In 10 of 19 chromatograms for the first Florisil eluant for aqueous and particulate phases of influent and discharges to storage at Muskegon, it represented 20% or more of the integrated peak area. In 3 of 8 chromatograms for incoming wastewater at Whitehall, the area for this peak represented 50 to 90% of the total for all monitored peaks.

The other two peaks, when encountered, appeared in varying proportion in all three Florisil eluants. The peak at 115-118 sec appeared more frequently at Muskegon than at Whitehall (peak area percentages greater than 20% in 8 of 57 chromatograms vs none greater than 20%, of 24 at Whitehall). The peak at 164-168 sec appeared mainly in the aqueous phase at Whitehall where it was the principal peak in the second Florisil eluant (28 to 95% of total area). When encountered at Muskegon, it was a minor peak (less than 10% of peak area in most cases) and was variously distributed between aqueous and particulate phases and among the three Florisil eluants.

The unknown peaks varied independently of each other and independently of peaks which might be assigned to major diagnostic PCB components of the common Arochlors. GC-MS scans of the first Florisil eluant for raw influent samples taken in 1976 have shown no evidence for the degree of chlorination required of PCB species in regions of prep chromatograms where they might be expected. Positive identification has been hampered by inadequate sample size and the number of parent species encountered (Pesticide Research Center, Michigan State University).

Thus, it appears that PCB's were not present in the substantial concentrations that might be inferred from these unknown peaks. Nevertheless, low concentrations may well have been present. Individual PCB species would have appeared at peak positions monitored for several pesticides which also appear in the first Florisil eluant (Table II-3, Appendix II). The probability for confounding is augmented further by the array of other organics which might have been expected from industry.

Persistent organochlorine insecticides --

Among the pesticides in Tables 39 to 43 are several organochlorine insecticides that were widely used prior to the mid-sixties. Persistent residues of aldrin, dieldrin, endrin, DDT, heptachlor and lindane were widely distributed in soils, waters and sediments (Edwards, 1973; Carey et al., 1976; Crockett et al., 1974; Glooschenko et al., 1976; Lake Michigan Interstate Pesticides Commission, 1972; Schacht, 1974). Manufacture and use of these chemicals in the U.S. and Canada have declined as more degradable insecticides became available. This has been reflected in declining frequency of encounter with these chemicals in surface waters since 1966 (Lichtenberg et al., 1970). Nevertheless, dieldrin and DDT, along with PCB's, are still considered to be the most widely distributed environmental pollutants in the Great Lakes Basin (Joint International Commission, 1976).

During the present decade, persistent organochlorine residues retained in soils and sediments continue to appear in streams during periods of heightened or turbulent flow associated with runoff or erosion from agricultural, residential or recreational areas (Miles, 1976; Miles and Harris, 1973; Snow, 1977; Truhlar and Reed, 1976). Frequencies and ranges of concentration reported in these studies were similar to those reported here for aldrin, dieldrin and endrin (Tables 47 and 48). DDT species were encountered more frequently in the cited studies than here, and maximum concentrations in two of the studies were 50 to 100-fold greater (Snow, 1977; Truhlar and Reed, 1976). Heptachlor and lindane or related species were encountered more frequently here than in the cited studies and at generally higher concentrations.

There is no evidence that any of these insecticides were produced locally during or immediately preceding the study period. If the GLC peak identifications given here are valid, the implicated compounds must have originated in areas of residual accumulation or current use. Concentrations in contributing runoff or stream flows would have had to be substantially greater than those encountered at treatment sites. Since more than 50% of the flows at the Muskegon site come from the paper mill, periodic concentrations in Muskegon Lake, double those in Tables 39 to 42, would suffice to explain the data. The cited stream load studies indicate that such concentrations are not unreasonable.

The only independent analyses found for direct comparison were for one sampling station near the outlet channel from Muskegon Lake to Lake Michigan (Station 610030, Comprehensive Studies Section, Environmental Services Division, Michigan Department of Natural Resources). These analyses are for seven samplings (36-hr collections) made at irregular intervals over the period from March 1971 through July 1976. All of the chlorinated hydrocarbon pesticides of concern here were searched for, but none were detected except for DDT species (12 ng/l) in the March 1971 sampling. Arochlors 1242, 1254 and 1260 were searched for, and 1254 was reported once at 37 ng/l (1971). Phthalates were searched for in 1974 and 1976, and DEHP was found at 2,000 to 3,000 ng/l in the one sample taken in 1974 and in one of two taken in 1976.

These data are non-supportive but do not preclude the probability that substantial concentrations of pesticides from non-point sources will be found from time to time in areas of the lake that receive direct discharges from streams and metropolitan storm flows. Concentrations associated with heavy runoff, turbulent flow in streams, or turbulence in areas of sedimentation within the lake itself, will be attenuated quickly by sedimentation (Edwards, 1973; Merkle and Bovey, 1974). Further attenuation will occur by numerous continuing processes: volatilization, concentration in aquatic biota and bottom sediments, biological and catalytic degradation, photochemical alteration, and dilution by more normal stream flows of low concentration (Kaufman, 1974; Matsumura, 1973; Sanborn, 1974).

Heptachlor, lindane and related species -- When encountered here, values for heptachlor and its metabolites (Heptachlor epoxide and 1-hydroxychlordene) and for lindane and other BHC isomers were often higher than reported over the period 1965 to 1969 in streams and surface waters of the

U.S. (Edwards, 1973) and much higher than most values reported over the period 1969 to 1972 in streams entering Lake Michigan (Lake Michigan Interstate Pesticides Committee, 1972; Schacht, 1974). Confounding with PCB's or other industrial organics may well have occurred. However, peaks for lindane were well separated from significant peaks in chromatograms run concurrently for Arochlors which might reasonably have been expected (1242, 1248, 1256, 1260).

Chronic inputs of heptachlor and lindane or technical BHC at point or nonpoint sources would be required to sustain levels indicated here. Heptachlor is converted rather quickly in soils to the epoxide or to 1-hydroxychlordene, both of which are subject to further alteration and degradation. Lindane and other BHC isomers are degraded rapidly under anaerobic conditions. Isomerization (conversion of one isomer to another) may also occur. There is evidence that β-BHC may accumulate as the most persistent isomer in areas where BHC has been used extensively (Kaufman, 1974; Matsumura, 1973).

Both heptachlor and BHC isomers are relatively volatile, and lindane is the most soluble of the persistent organochlorine insecticides (Biggar and Riggs, 1974; Edwards, 1973). It would be expected that local concentrations associated with current use would be diluted rather quickly by dispersion into the general environment. Nevertheless, insecticidal activity associated with these compounds persists in soils for periods of 2 to 3 years. The compounds themselves can be retained in soils and sediments for much longer periods of time and can be found in streams receiving runoff from areas treated several years earlier (Hiltbold, 1974; Merkle and Bovey, 1974).

Concentrations of BHC isomers 10-fold greater than reported here have been observed in streams receiving heavy runoff from forest areas sprayed one and two years earlier with BHC (Jackson et al., 1974). A concentration of 170 ng/l had been found four years after an earlier spray treatment.

Both lindane and technical BHC are used for insect control in Christmas tree plantations which occupy significant acreages in Muskegon County, in the immediately adjacent counties in the Muskegon River basin (Newaygo) and the White River basin (Oceana), and in Missaukee and Wexford Counties in the upper basin of the Muskegon River (Manthy et al., 1973; Wallner, 1975). Lindane and heptachlor are active ingredients in proprietary products that are widely distributed for use by homeowners and landscape services on trees and other ornamentals. Important uses call for spray applications in spring or early summer or in the fall, although applications may be made at any time during the growing season.

In 1974, twice-normal rainfall was reported each month from April through August at one or more stations in the immediate tri-county area (stations at Hart, Hesperia, Muskegon and Newaygo). Rains through the balance of 1974 were less than normal at most stations (NOAA, 1974).

The coincidence of high rainfall with the spring and summer season of spray application would explain the frequency and level of encounters with heptachlor and metabolites and with lindane and other BHC isomers at Muskegon during this period (Tables 39 and 41). Entry into wastewater flows could have occurred by runoff from areas of current use or residual accumulation or directly through drift, accidents or inappropriate disposal.

Wintertime encounters in 1974 (Tables 39 and 41) or in 1975 (Tables 40 and 42) could be expected from runoff due to a combination of snowmelt plus rain which often occurs in this part of Michigan.

Spring rainfall in 1975 was less than normal until May when higher than normal precipitation was reported for stations in the upper basin of the Muskegon River. Rains were more general in June, with near twice-normal totals in the immediate tri-county area. Heavy rains over the entire region in August resulted in totals 2- to 4-fold greater than normal at all stations in the Muskegon River and White River basins (Cadillac, Lake City, Higgins Lake, Houghton Lake, Big Rapids, Evart, Hesperia, Muskegon). September and October were dry, but rainfall 50 to 100% greater than normal was again reported in November at most of these stations.

Encounters with lindane from May to September 1975 (Tables 40 and 42) could have originated in areas of residual accumulation or current season's use. Sharply increased concentrations in October and the appearance of α-BHC and heptachlor suggest origin in drift, runoff or other direct inputs associated with current fall spraying operations. These unusually high concentrations in October would have been associated also with reduced volume of stream flow after several weeks of dry weather with consequent lesser dilution. The later appearance of heptachlor epoxide in November (Table 40) and December (Table 42) suggests a period of exposure to soils and points to origin in runoff from areas of earlier application.

The above relationships to probable uses and climatic conditions in river basin areas support the identifications given here. Quantities distributed through wholesale or retail channels are not known since sales of lindane, BHC or of the proprietary products containing heptachlor are not reported. Heptachlor is a restricted use pesticide. As such, sales for agricultural uses have been reported since 1972 by dealers licensed under Regulation 633 of the Michigan Department of Agriculture. The reported sales have been mainly for use on grains and forages and have not exceeded 1 metric ton annually statewide. Negligible quantities have been reported for counties in the White River or Muskegon River basins (annual summaries of restricted use pesticide sales, 1972-1976, Plant Industry Division, Michigan Department of Agriculture).

Aldrin and dieldrin -- Usage of aldrin and dieldrin declined during the late sixties in Michigan, as elsewhere in the U.S. However, sales increased again when uses of DDT were banned in the state in 1969 and nationwide in 1972. The following sales have been reported by licensed restricted use pesticide dealers in Michigan:

	Licensed sales (metric tons)	
	Aldrin	Dieldrin
1972	13.2	5.3
1973	22.5	13.8
1974	24.9	11.0
1975	3.3	2.0
1976	.07	.4

In 1974, 18 metric tons of aldrin (70% of the state total) was sold in one county in the upper Muskegon River basin. Of the dieldrin in 1974, 37% was sold in 9 counties which lie wholly or in part in the basins of the Muskegon and White Rivers. Rapidly diminishing quantities have moved from stocks on hand since U.S. registrations for both chemicals were cancelled in 1975. Intended uses reported by dealers were for aldrin mainly on grains and forages and for dieldrin mainly on fruits and vegetables. Lesser uses for both compounds were for ornamentals, forest and Christmas trees, and "other uses."

These figures give only an approximate indication of actual use since these river basins do not define a merchandising area. Also it is likely that stockpiling occurred after the first rebuttable notice of cancellation was announced in 1971. Nevertheless, the reported sales indicate that significant quantities were used in 1973 and 1974 and probably also in 1975.

Aldrin was encountered in wastewaters only three times. A questionable detection at Muskegon in February 1975 (Table 40) is supported by its detection a month later in discharges to storage (Table 42). It was detected only once at Whitehall, in September 1975 (Table 43).

Dieldrin was not encountered at Whitehall. It was observed entering storage lagoons at Muskegon in August 1974 (Table 41) and in irrigation water coming out of storage a month later (Table 44).

The most probable sources for aldrin would have been in areas of current or recent application since aldrin is converted quickly in soils to dieldrin. Current or recent applications would likely have been required, also, for dieldrin to appear. The probability that dieldrin could have originated in persistent older residues is remote since it is usually found in soils and sediments at much lower concentrations than DDT (Edwards, 1973; Carey et al., 1976; Crockett et al., 1974; Roan, 1975). Neither aldrin nor dieldrin was found in the same monthly composites with DDT species or endrin. The latter compounds would have originated, almost necessarily, from applications made prior to 1972 and probably earlier.

The encounters with dieldrin in wastewaters came after unusually heavy rainfall in the Muskegon River basin from April through August 1974. The encounters with aldrin in 1975 were associated with unusual sales in the region in 1974 and occurred during the late winter to early spring runoff period in 1975 or after 2- to 4-fold greater than normal rainfall in August.

It is significant that the indicated levels of use did not result in chronic appearance or high concentrations of aldrin or dieldrin in wastewaters. The relation to sales reported in contributing river basin areas gives a rough indication of the extent to which pesticides of low solubility and designed primarily for soil application may appear at these treatment sites. Reported sales in Michigan of aldrin and dieldrin during these last few years before cancellation can provide a useful reference for evaluating the residual environmental impact of dieldrin in the Great Lakes Basin.

DDT species and endrin -- Negligible quantities of DDT or endrin were sold in Michigan from 1972 to 1976 and none in the nine watershed counties of the White River and Muskegon River basins where significant non-point sources might exist (Clare, Mecosta, Missaukee, Muskegon, Newaygo, Oceana, Osceola, Roscommon, Wexford). Permissible uses remain for DDD (TDE) on fruits and vegetables, but sales statewide were less than 2 metric tons in 1972 and 1973 and declined sharply to less than 200 kg in 1975 and 1976. No sales of DDD were reported in the above listed counties.

It is unlikely that insecticides containing endrin or DDT species (other than DDD) have been used in significant quantities during the present decade in Michigan. Prior to the mid-1960's, DDT was for two decades the most widely used insecticide in agriculture and forestry as well as in urban and recreational areas. Combined sales of aldrin plus dieldrin had overtaken sales of DDT in the U.S. by 1965 (Edwards, 1973).

The relative cumulative impact of usage prior to 1970 is reflected in soil residues reported in synoptic surveys made in 1970 (Carey et al., 1976; Crockett et al., 1973). At 54 cropland sites in Michigan, DDT species and dieldrin were encountered with equal frequency (7 of 54 sites), but the mean concentration for total DDT species was 50-fold greater than for dieldrin (530 vs 10 ng/g), and the maximum concentration was 100-fold greater (25,590 vs 220 ng/g). At 23 urban sites in Muskegon's metropolitan neighbor, Grand Rapids, dieldrin was not detected in 1970, but DDT species were found at 19 sites in concentrations up to 6,660 ng/g, with a mean of 660 ng/g.

Most frequently encountered in 1970, and at highest concentrations, were p,p'-DDT and p,p'-DDE, but p,p'-DDD was also found as well as all o,p isomers. Neither aldrin nor endrin was encountered in Michigan, but both were found occasionally at agricultural sites elsewhere in the country.

DDT species continue to be the most frequently encountered chlorinated hydrocarbons in soils. Concentrations up to 20,000 ng/g have been reported in national surveys as recently as 1974 (Roan, 1975). Such high values are unusual, but their continuing appearance in surveys is evidence that localized high residue concentrations persist in areas of discontinued use.

All of the persistent chlorinated hydrocarbons have been reported in runoff, sediments or stream flows associated with agricultural, urban and recreational areas. DDT species continue to be found with greatest frequency and at much the highest concentration as recently as 1974 (Roan, 1975) and 1976 (Snow, 1977). Concentrations reported for DDT species in streams during base flow or normal runoff events are lower than reported here for wastewaters (Miles, 1976; Miles and Harris, 1973; Minnesota Pollution Control Agency, 1971). Occasional concentrations 10- to 100-fold greater than reported here have been reported for storm events when suspended sediments were high due to erosion or turbulent stream flow (Snow, 1977; Truhlar and Reed, 1976).

The parent DDT species tend to be protected against alteration in soils and may be the dominant species in runoff from land surfaces. Runoff and erosion expose soil residues to a wide range of aerobic to anaerobic environments in streams. Both DDE (aerobic metabolite) and DDD (anaerobic metabolite) tend to increase relative to DDT in bottom wash sediments over time and with distance downstream from the source (Miles, 1976; Miles and Harris, 1973). The ratios DDE:DDT:DDD will reflect the quality of water in a given stream as well as stream geometry conducive to greater or lesser aeration or disturbance of bottom sediments (Snow, 1977).

In the present study, p,p'-DDE was encountered at concentrations up to 345 ng/l at Muskegon during April and May of 1974 (Tables 39 and 41). Earlier snow accumulations were greater than normal, and twice-normal precipitation was reported for March, April and May at individual stations in the immediate tri-county area. The presence of DDE isomers was indicated twice in 1975, once in association with spring runoff in April and again in September after 2- to 4-fold greater than normal rainfall in August (Table 42).

DDD was encountered only once--at Whitehall in April 1975 at 400 ng/l (Table 43). Again, the absence of peaks for other DDT species suggests origin in suspended bottom sediments. Since DDD is formed during anaerobic metabolism, this would imply that bottom environments in the White River or its tributaries are less well aerated than in the Muskegon River or in areas of sedimentation in Muskegon Lake where disturbance can occur by wave action or by heavy stream discharge. It is possible also that DDD (TDE) may have been used recently on fruits or vegetables in the White River basin, although no sales have been reported in the area since 1972.

Unaltered DDT was encountered only once--in January 1975 at Muskegon (Table 40). It may have been accompanied at this time by endrin which was indicated in discharges to storage (Table 42). Both could have originated in runoff due to snowmelt plus rain, perhaps from areas where unusual residue accumulations had been exposed to erosion by a change in management as, for example, new construction or subdivision development.

The identification here of peaks for endrin and DDT species in wastewaters is supported by their association with weather conditions conducive to heavy runoff, erosion and turbulent stream flow in contributing watersheds. The most probable mode of entry would be through wastewater discharges from industries that take feedwaters from lakes or streams. This would imply that concentrations in surface waters near points of intake for the paper mill at Muskegon may, at these times, have been double those observed at the treatment site. The cited literature indicates that this is not an unreasonable expectation. The proportional contribution from the tannery at Whitehall is not known, but it is considered a major contributor since it connected to the system in late 1974. In both systems, direct inputs from interconnected storm flows or through sewerage failures in areas of flooding may have occurred also.

Less persistent pesticides --

A number of less persistent pesticides in current use were encountered in incoming wastewaters at concentrations of 10^2 to 10^4 ng/l. These included 2,4-D esters, phorate (Thimet^R), diazinon, dimethoate, Lasso^R and Vegadex^R (CDEC).

2,4-D esters -- Ester formulations of 2,4-D are used for control of broadleaved weeds in small grains, forage legumes, pastures, along fencerows, ditchbanks, highway rights-of-way, and appear in proprietary products for use on turf. Applications are normally made in spring or fall. The chemicals are degraded rather rapidly (1 to 5 weeks). Encounters were consistent with applications in spring or fall and with carryover from late spring or early summer applications to periods of heavy runoff in August or from late fall applications to periods of winter snowmelt or early spring runoff (Tables 39 to 43). Appearances in July, August, or September could have come from summer applications for control of woody brush species along ditchbanks, in which case the 2,4-D esters would likely have been accompanied by 2,4,5-T. Peaks for 2,4,5-T were not monitored.

The methyl ester was encountered most frequently at Muskegon (Tables 39 to 42). The isopropyl ester was indicated most frequently at Whitehall (Table 43) but appeared at Muskegon only in 1975 (Tables 40 and 42). Patterns of merchandising and use might account for such variations in frequency for the different esters, but actual sales or usage are not known.

Phorate (Thimet^R) -- Peaks for phorate were first encountered at Muskegon in December 1974, but were found in 7 of 12 influent composites in 1975 (Tables 39 and 40) and in three samples of discharge into storage (Table 42). Phorate was not encountered at Whitehall.

As a systemic insecticide, phorate has limited used on vegetable crops. It is used for control of corn rootworm, and there may have been a substantial increase in 1975 due partly to cancellation of aldrin and partly to entry into the area of the western corn rootworm with developed resistance to the chlorinated hydrocarbons (Ruppel, 1975).

However, the uses of phorate involve placement in soil before or at planting time or at the time of first cultivation. Also, phorate is quickly degraded in soil (persistence, about 2 weeks). Parathion, which is only slightly less persistent than phorate, was never detected in wastewaters, although it is much more widely used for both soil and foliar applications (sales of parathion reported by restricted use pesticide dealers in 1974 and 1975 were about 50 metric tons statewide). Thus, the chronic appearance of phorate through 1975 cannot be explained by usage.

Major production of phorate by a chemical company on Black Creek appears not to have been undertaken until early 1976. Whether pilot production may have been undertaken earlier is not known. Processing discharges from this plant were not diverted to the county sewage collection system until May 1976. The company did report two episodes of holding lagoon failure in April and in August 1975 (Muskegon Chronicle, December 21, 1975). These were associated with fish kills in Black Creek and Mona Lake. Phorate was not analyzed for in samples of discharges, lagoon seepage or fish taken during this period by state water quality control personnel.

The known circumstances are inconclusive. If phorate had in fact been present in these accidental discharges, it could have entered wastewater flows through industries that take their feedwaters from Black Creek or Mona Lake. The proportion of total flow originating in these industries is not known. If it were as much as 1%, a 100-fold dilution might have been expected at the treatment site. This would imply that chronic concentrations of the order of 10^5 to 10^6 ng/l were maintained in Black Creek and Mona Lake for periods of months after each discharge. Whether this is a reasonable expectation is uncertain since the persistence of phorate in sediments or subsurface seepage is not known. Phorate itself is soluble to the extent of 5×10^7 ng/l (50 ppm).

Confounding of phorate and α-BHC may have occurred in quantitation on the OV-17/QF-1 column. However, these two species are differentiated by RF values and by color on thin layer chromatograms which were used for confirmation with all extracts (Appendix II). Peaks for these compounds are clearly separated on a DEGS column which was used, in addition to routine confirmation on QF-1, with several extracts where both phorate and α-BHC were indicated. The possibility remains that unknown industrial organics may have interfered with these determinations. These uncertainties emphasize the need for back-up analytical capability for positive confirmation of presumptive identifications based on chromatographic parameters.

Diazinon -- Diazinon has extensive uses involving soil and foliar applications on field crops and horticultural crops. As in the case of phorate, soil applications for control of corn rootworm increased sharply about 1975. Spray applications for control of the six-spotted leafhopper (vector for aster yellows) for several vegetable crops must extend over field margins and ditchbanks for effective control. In muck soil areas these applications are frequently made from the air, increasing the likelihood for direct entry into surface waters. Applications must be repeated every 3 to 6 days.

In spite of extensive usage and the vulnerability of surface waters to contamination, diazinon was encountered infrequently in wastewaters at Muskegon (Table 47) and was not detected at Whitehall (Table 43). Concentrations in the ppb range (10^3 ng/l) were indicated for raw influent in association with unusually heavy rainfall in August 1975 (Table 40) and in discharges into storage in January 1975 (Table 42). The wintertime encounter is not inconsistent with the accepted persistence for this compound (3 months in soil under growing season conditions).

Dimethoate -- Identification of peaks for dimethoate at Muskegon (Tables 40 and 42) and at Whitehall (Table 43) is to be questioned, since the reference chemical was not recovered from Florisil (Appendix II, Table II-3). There are reasons to expect that it might appear. In addition to uses in production of crops and ornamentals, dimethoate is used as a residual insecticide around farm buildings, homes and commercial establishments. It is the material most commonly used in the custom pest control industry for fly control. It is among the most soluble pesticides (2 to 3% in water). Residues picked up in cleaning water would likely be dumped directly into sanitary drains and might well appear in wastewaters associated with seasonal cleaning or renovating in homes, stores, warehouses, etc.

Encounters with peaks assigned to dimethoate in fall, winter and spring would be consistent with this expectation. However circumstantial inference must be discounted, since analytical protocol was inappropriate for this chemical.

Lasso^R (alachlor) -- This herbicide is used as a preemergence surface spray for control of emerging broadleaved weeds and annual grasses. Probably the only crops in contributing watershed counties on which it may have been used would have been field corn, sweet corn and potatoes.

Lasso is readily degraded in moist soil but may persist for considerable periods in dry soil. Following a drier than normal early season in 1975, the presence of Lasso at concentrations in the ppb range was indicated in discharges to storage in July after heavy rains in June in areas near Muskegon (Table 42). After basin-wide heavy rains in August (2 to 4 times normal), similar concentrations were indicated for both influent and discharges to storage (Tables 40 and 42). Encounters in November and December were again associated with widespread heavy rains in November.

The previous season (1974) was wetter than normal through August. This would have promoted more rapid dissipation of Lasso. However, weather records reflect a scattered distribution until August when heavy rains were general in the immediate tri-county area. Peaks for Lasso were not found for influent, but 12 ppb was indicated in September discharges to storage (Table 41).

Circumstances of weather in relation to use practices support the indentification given here.

Parathion (ethyl and methyl) -- Ethyl parathion was not encountered at any time. Methyl parathion was indicated at levels below reliable quantitation on one occasion at Muskegon (Table 41).

Failure to detect parathion is significant since ethyl parathion is the most widely used of the restricted use pesticides. Fifty metric tons were sold in 1974 and 1975, mainly for use on fruits and vegetables but with significant usage on grains, forages and ornamentals. Less than 2 metric tons of methyl parathion were sold, mainly for use on vegetables.

Parathion is used in many of the same areas and frequently in the same tank mix with diazinon. Direct entry into surface waters can occur from spraying of field margins and ditch banks or from aerial sprays in muck soil areas. Diazinon, with a persistence in soil of 3 months, was detected infrequently. Failure to detect parathion reflects its susceptibility to rapid degradation (persistence in soil, about 1 week).

Vegadex^R (CDEC) -- This is not a widely used herbicide but is used in preemergence sprays for control of emerging annual weeds in certain vegetable crops and ornamentals. It is more persistent than parathion (about 6 weeks in soil). The appearance of peaks for Vegadex in influent at Muskegon in April 1974 coincides with the season of most probable use (Table 39) and with unusually heavy rainfall in the immediate tri-county area.

Pre-chlorination Flows and Irrigation Water (1974)

Samples of water after the storage phase of treatment were obtained only during the summer and fall of 1974 (Table 44). Six samples of pre-chlorination flows were taken and 7 at irrigation pumps--not enough to draw any inferences regarding effects of chlorination. The 13 observations, as a group, can be compared with data for incoming wastewaters in 1974 (Tables 39 and 41) to draw some tentative inferences regarding effects of storage.

Heptachlor (and/or its metabolites) and *p*,*p*'-DDE were observed entering storage at concentrations of the order of 10^2 ng/l. Only p,p'-DDE and 1-hydroxychlordene were detected in waters out of storage, both at greatly reduced concentrations. Lindane and/or isomers were found with similar high frequency before and after storage (Table 47). In 17 samples of incoming wastewater where BHC isomers were detected in 1974 (Tables 39 and 41), their mean sum was 163 ng/l. The mean sum for 7 of 13 samples coming out of storage (Table 44) was similar (134 ng/l). DEHP was detected less frequently after storage (Table 47), and concentrations were substantially lower than maximum concentrations before storage (Table 48).

These comparisons indicate that significant quantities of *p*,*p*'-DDE, heptachlor and metabolites, and DEHP were removed from wastewater flows during storage. Such losses could have occurred by degradation, volatilization or retention in sediments. The benzene hexachlorides, as a group, were not attenuated, although some isomerization may have occurred. For example, β-BHC was not found in incoming wastewater but was indicated in water coming out of storage lagoons in November (Table 44). This would be consistent with reports that β-BHC may accumulate differentially as the most persistent isomer (Kaufman, 1974; Matsumura, 1973).

Single observations for dieldrin, Lasso and Vegadex do not allow for inferences drawn from the data. Dieldrin would be expected to persist, whereas the acetanilide and the carbamate might well be degraded extensively or removed into sediments during storage.

Outfall Waters

General hydrologic considerations --

The area occupied by the Muskegon wastewater management system included what was formerly the upper reach of Black Creek. In preparing the site, drainage patterns were altered so that some areas which formerly drained to Black Creek and then to Mona Lake now drain to the north outfall on Mosquito Creek, which is a tributary of the Muskegon River.

The system also intercepts Cranberry Creek and two large county drains (Hall Drain and Big Drain). The intercepted drainage originates in agricultural areas east of the site, including a substantial area of drained organic soils in Moorland Township. The organic soils and associated artificially drained mineral soils are used for production of vegetables and cash crops (National Cooperative Soil Survey, Muskegon County, 1968). This off-site drainage has been diverted to pass through the site via an open ditch which discharges into Black Creek at a point west of the site.

The extent to which off-site drainage was, in fact, isolated from on-site drainage collected to either of the outfalls during the period of this study is not known. Routine monitoring by management system personnel indicates that input chloride is diluted in the system, but this has been attributed to precipitation and groundwater intrusion.

Underdrainage from about two-thirds of the irrigated circles is now directed to Mosquito Creek (the north outfall). Drainage from the southern third of the site is directed to the Black Creek outfall. The soils in this southern third are somewhat less permeable than those to the north and are inadequately drained by tile at 500 ft spacing (150 m). As a result, they have accepted less water. During the period of this study, the south-draining circles received wastewater at the rate of 0 to 130 cm over a 25 to 30-week season each year, as compared with 130 to 190 cm on most circles to the north. Some of the north-draining circles received 250 cm or more (USEPA, Region V, 1976).

These differences in drainage area and wastewater loadings are reflected in summertime flows at the two outfalls: 33 to 35 MGD at the north outfall, 5 to 8 MGD at the south (Municipal Wastewater Surveys for August 26-27, 1975, and July 6-7, 1976, Muskegon Wastewater Management System No. 1, Michigan Water Resources Commission).

Total flow for the two outfalls was about 40 MGD, which compares with 28 MGD of wastewater being received at the time of the two surveys. This difference between inflow and outflow is reasonable since approximately 50 MGD must be applied over a 7-month irrigation season to dispose of 12 months' influent. Drainage during the summer will normally be less than input due to evapotranspiration and consumptive use by the crop.

Chemicals encountered --

Monthly composites of drainage at the two outfalls at the Muskegon site were monitored, beginning April 1974 (Tables 45 and 46). The outfall on Silver Creek at Whitehall was not monitored.

Two composites were taken before the first application of wastewater was made in the latter half of May 1974. The only chemical encountered in quantifiable concentrations was Lasso^R. Encounters at both outfalls could have originated in soil residues from earlier use by private operators on the site, although Lasso had not been detected in background soil samples. It is possible, at this early stage of design implementation, that agricultural chemicals could have entered the system in off-site drainage from the east.

Lasso and atrazine were used each year for weed control on essentially all of the irrigated acreage on the site. The principal encounters with Lasso in drainage were associated with planting (May) and the early growing season (Tables 45, 46). Lasso encountered at other times could reasonably have entered in wastewater (cf. Tables 40 to 42).

Peaks for atrazine were not observed in incoming wastewater. One encounter in drainage at the north outfall in September 1974 (Table 45) can be ascribed to leaching of applied atrazine under conditions of heavy hydraulic loading on north-draining circles. A number of these were irrigated at rates greatly in excess of design because less than 30 of the 52 circles were operational by the beginning of the 1974 season, and storage lagoons were dangerously full.

Diazinon was used on site in 1974 as insurance against corn rootworm. Its appearance in quantifiable concentrations at the north outfall in October and November 1974 (Table 45) can be ascribed to this application. Diazinon was not used on site in 1975, but peaks for it were observed in incoming wastewater (Tables 40, 42). It was not detected at outfalls in 1975.

Sutan^R (butylate) was used on some circles in 1975 for control of nutsedge. It could not be confirmed satisfactorily in sample extracts because of interference from contaminants with similarly short retention times (R_t relative to aldrin = 0.23 on OV-17/QF-1).

Peaks for aldrin and dieldrin were observed in drainage during the early growing season of 1974 (Tables 45, 46). Because of the large regional sales reported in 1973 and 1974, these restricted use pesticides may well have been present in wastewater which had been accumulating in storage lagoons since June 1973. Dieldrin, but not aldrin, had been indicated also in background samples of surface and subsoils (Tables 50, 51, 52). The very low levels of residual dieldrin in soils would not account for finding 31 ng/l at the north outfall in July 1974, however (Table 45). Localized areas of higher soil residues may well have existed in association with former residences or earlier farming operations. However, input wastewater would have been the more likely source for this level of breakthrough into drainage. Heavy irrigation during the early weeks of operation in 1974 would have favored rapid downward displacement of chemicals from both wastewater and soil sources.

Quantifiable concentrations of p,p'-DDE were indicated in 35 of 49 background samples of soil (Tables 50, 51, 52) and in incoming wastewater in April and May of 1974 (Tables 39, 41). Levels approaching the quantifiable limit were detected at the north outfall from April through July 1974 (Table 45) and at the south outfall just after irrigation was initiated in May 1974 (Table 46). Disturbance of soils during site preparation may well have exposed sites of residual accumulation to leaching under conditions of heavy local rainfall in March, April and May, followed by the period of unusually heavy irrigation on the limited number of circles that were operational at the beginning of the 1974 season. The indicated presence of p,p'-DDE in the applied wastewater would have contributed, also, to breakthrough at outfalls.

Heptachlor and/or its metabolites (heptachlor epoxide, 1-hydroxy-chlordene) were indicated in quantifiable concentrations at outfalls only in July 1974

(Tables 45, 46). Peaks for one or more of these species had been present in 9 of 10 samples of incoming wastewater composited from April through July (Tables 39, 41). Frequencies of encounter at the two outfalls are consistent with earlier and heavier irrigation on north-draining circles than on circles draining to Black Creek.

Heptachlor and its metabolites have not appeared in credible concentrations at outfalls since July 1974, even though concentrations of the order of 10^2 to 10^3 ng/l have been indicated for incoming wastewater through 1975 (Tables 40, 42). There is evidence in background soil analyses that heptachlor may have been used on site in the past (Tables 50, 51, 52). Thus, microbial populations adapted to metabolizing heptachlor and derivative intermediates may have been present before wastewater was applied. These species are also adsorbed strongly by soil organic colloids. Thus, interception by adsorptive and degradative processes would account for their virtual absence in drainage except when they were ostensibly present in wastewater applied at excessive rates.

Lindane and/or other BHC isomers were encountered frequently at outfalls from the time irrigation was initiated in 1974 through early spring of 1975 (Tables 45, 46). Scattered occurrences since then have been at or below limits of quantitation. However, indicated inputs in wastewater did not decrease in frequency or concentration from 1974 through 1975 (Tables 39 to 42).

Lindane or its isomers were not detected in background samples of soils. Enzymatic competence to degrade BHC species would not have developed in their absence. The data suggest that adaptive populations may have developed in soils after BHC species were first introduced with wastewater in 1974.

A further consideration is the larger annual production and return of plant residues from irrigated corn, as compared with that from native cover, stressed for water and nutrients, that existed on substantial portions of the site before present management was imposed. Thus, an increased rate of turnover of organic matter can be expected to lead to an increasing organic content in soils that were initially low in organic content. With irrigation, it can be expected that stabilized humic materials will be distributed to greater depth in the profile also.

It is early to assess these expected changes with confidence because of the very great variability introduced by land clearing and leveling operations. Organic carbon has increased in surface soils and subsoils in a number of north-draining circles. As has been noted, irrigation commenced earlier in north-draining areas of the site, and loadings have been consistently heavier than in areas which drain to Black Creek. Increased organic content in the soil mantle will increase interception of both organic and mineral species by adsorption and complexation.

Other pesticides which have been indicated occasionally at outfalls (Tables 45, 46) have also been encountered in incoming wastewater (Tables 39 to 42). These include Vegadex^R (CDEC) and three 2,4-D esters (butyl, isobutyl, isopropyl). The methyl ester of 2,4-D was not detected at outfalls, although peaks for it were found in raw influent on several occasions in 1974 and 1975

(Tables 39, 40). It was not detected in discharges to storage after pretreatment (Tables 41, 42) but was indicated in soils in 1975 (Tables 54 and 55). None of these herbicides has been used on site since the land came under county control.

The industrial chemical, DEHP appeared at outfalls in detectable concentrations (10^3 to 10^5 ng/l) at times when a substantial proportion of the irrigated acreage was being subjected to exceptionally heavy hydraulic loading. Thus, it appeared in late May, June and July of 1974 when water had to be dumped on 20 or 30 operational circles to lower dangerously high water in storage lagoons. It appeared again at the north outfall in September 1975 after 21 cm (8.3 inches) of rain in August, combined with normal irrigation, resulted in total water inputs of 40 to 50 cm (averaging 10 to 13 cm per week) on most of the circles draining to the north (operational data, Muskegon County Wastewater Management System).

In 1975, irrigation was discontinued (for periods of 3 to 6 weeks on individual circles) to accommodate grain harvest in September and October. After this interruption, heavy irrigations were employed (10 to 15 cm/week on many circles) to empty lagoons for winter storage. These season-end applications were accompanied by the appearance of DEHP at both outfalls in November or December.

Except during these periods of excessive hydraulic loading, DEHP has been reduced by passage through the system, from incoming concentrations of 10^4 to 10^6 ng/l to less than 10^3 ng/l (the limit of quantitation) at outfalls. Changes in frequency of detection and in ranges of concentration at sampled flow points (next section) indicate that removals of DEHP occurred both in storage and during passage through soil systems.

Frequencies of Occurrence and Ranges of Concentration in Waters

Frequencies and ranges of concentration for trace organics detected by GLC/ECD in waters associated with the Muskegon system are summarized in Tables 47 and 48.

Chemicals encountered most frequently in incoming wastewater were lindane (or isomers), heptachlor (or metabolites), and the industrial chemical, diethylhexylphthalate (DEHP). Frequencies of encounter and maximum concentrations give no evidence of change from 1974 to 1975 in the chronic nature of input for these compounds. There is no evidence that influent levels were reduced by aeration and settling. In fact, there is a suggestion that extractability may have been increased by physical or metabolic comminution of occluding structures (tissue fragments, fibers, floc, etc.).

Data for flows after storage (obtained only in 1974) indicate that heptachlor and heptachlor epoxide were removed during lagoon storage and that the flux of 1-hydroxychlordene and DEHP out of storage was reduced substantially from input (cf. Tables 39, 40, 44). By contrast, the frequency of BHC isomers, as a group, and their summed concentration did not change materially (the mean sum for BHC species in 17 samples before storage was 163 ng/l vs 134 ng/l for 13 samples after storage). The spectrum of isomers was different after storage.

Levels detected at outfalls will reflect dilution by precipitation and by waters entering from underlying aquifers or from intercepted off-site drainage. However, the virtual disappearance of heptachlor and its metabolites from drainage after July 1974 indicates that these compounds are being removed effectively in the system, whether in lagoons or in soils or both. The virtual disappearance of BHC isomers at outfalls since early spring of 1975 indicates a marked increase in interception over the first year of operation (Tables 45, 46).

As noted in the previous section, DEHP appeared at outfalls during periods of heavy hydraulic loading. Analytical sensitivity for this chemical was two or three orders of magnitude less than for chlorinated species. Concentrations less than 10 ppb would not have been detected. Nevertheless, changes in frequency and concentration in 1974 (Tables 47, 48) indicate that removals of DEHP occurred both in lagoons and in soils. Interception in sediments and soils would be expected, since phthalates are not exotic to natural systems. They are found among biosynthetic products of plants and microorganisms and in stable complexes with humic acids (Ogner and Schnitzer, 1970). Enzymatic competence to degrade simple aromatics is widely distributed (Alexander, 1977).

Thus, it is to be expected that DEHP will be removed efficiently from wastewaters if given sufficient residence time in lagoons or in soils. Chronic inputs should result in enrichment of sediments and soils with competent organisms and, consequently, in more rapid degradation. As management operations are routinized to avoid periodic excesses in wastewater application, episodes of breakthrough at outfalls should decline. Increased production and return of crop residues should contribute to increased interception by products of humification and to increased size and diversity of competent populations. Increased vigor of the vegetative cover will serve, also, to reduce net percolation and increase retention times during seasons of active growth.

Three pesticides used in connection with farming operations on the Muskegon site were encountered at outfalls. These were diazinon, atrazine and Lasso^R. A fourth (Sutan^R), used only in 1975, may have been present on occasions, but the corresponding peak could not be resolved credibly by the methods employed. Diazinon and Lasso were input, also, with wastewater.

Principal encounters with Lasso at outfalls were associated with planting and the early growing season, whereas credible peaks for diazinon and atrazine occurred later in the season and only in 1974 (Table 45). Atrazine would not have been detected at concentrations less than 1 ppb (Appendix II, Table 2). Nevertheless, the data suggest that Lasso was intercepted less effectively by soil materials than the other two pesticides under conditions of heavy hydraulic loading.

On the other hand, peaks for Lasso were encountered less frequently at outfalls in 1975 than in 1974 in spite of an indicated greater frequency in incoming wastewater (Tables 47, 48). This result would be consistent with developmental changes leading to more effective interception in soils. A more rational irrigation regime in 1975 and more vigorous growth of corn would have been contributing factors.

Other pesticides encountered at outfalls would appear to have originated primarily in wastewaters (aldrin, dieldrin, DDT species, phorate, 2,4-D esters, Vegadex^{R}). Others indicated in wastewater but not detected at outfalls were endrin, dimethoate, 2,4-D(ME) and 2,4-D(BE)I.

The various esters of 2,4-D are rapidly hydrolyzed in soils and sediments (Loos, 1975). For the esters to appear at outfalls, it would be necessary for them to pass through the system quickly.

The secondary butyl ester, 2,4-D(BE)II, was encountered most frequently at outfalls and at highest concentration. Encounters at the north outfall (Table 45) were during periods of heavy hydraulic loading, at which times 2,4-D(BE)II was associated with other trace organics, notably Lasso. A single appearance at the south outfall in December 1975 (Table 46) was associated with heavy rains and breakthrough of DEHP in November.

There is experimental evidence that different ester derivatives of 2,4-D vary in their susceptibility to hydrolysis (Aly and Faust, 1964). Failure to detect 2,4-D(ME) at outfalls, in spite of relatively frequent encounters in incoming wastewater, suggests that the methyl ester may have been hydrolyzed more rapidly in the system than the others.

Unfortunately, the peak for the free 2,4-D acid was not monitored. It is known that adaptive populations develop in soils and sediments amended repeatedly with 2,4-D (Aly and Faust, 1964; Loos, 1975). Degradation by adapted populations is rapid, and the adapted populations can persist for periods of months or longer in the absence of 2,4-D in the substrate. Adaptation to 2,4-D frequently confers competence to degrade related aromatics such as 2,4,5-T. Thus, the indicated periodic inputs of 2,4-D may, in fact, be beneficial for inducing and maintaining a broader range of enzymatic competence in soils.

Data for "unknown" peaks have not been tabulated. The compounds responsible for unreferenced peaks monitored in 1975 may be sufficiently exotic that degradative capability will, at best, be slow to develop. Two or more of the three peaks appeared in nearly all outfall samples. The indicated concentrations were reduced substantially from input, but peak areas as percent of the total for all monitored peaks tended to increase. Thus, the unknown chemicals may be more persistent or more mobile than many of the chemicals responsible for referenced peaks.

The data summarized in Tables 47 and 48 indicate that the Muskegon system has operated most effectively to intercept organics that are strongly adsorbed by soils or sediments (endrin, heptachlor, DDT, dieldrin, and related species) and chemicals that are readily metabolized (dimethoate, phorate). There is evidence of improved performance in the second year of operation over the first in removal of several relatively recalcitrant compounds input during farming operations on site or, at ppb to ppm levels, in wastewater (BHC isomers, diazinon, atrazine, Lasso).

The effectiveness of wastewater renovation with regard to trace organics can be expected to improve as irrigation regimes are rationalized and as agronomic limitations are identified and corrected. A questionable operational practice is that of discharging wastewater through disconnected sprinkler headers in spring and fall. Channeling of percolate through a severely restricted soil volume may have contributed to breakthrough of a number of chemicals into drainage at these times.

It is probable that industrial wastes include potentially hazardous organics that are more recalcitrant or more mobile in soils than DEHP or the pesticide species monitored here. For this reason, it appears important to utilize the total soil area accessible to the sprinkler system at all times.

Particulate-Phase/Aqueous-Phase Distributions

The fate of trace organics adsorbed on particulate matter will be closely linked with the fate of solids in the waste. Removal of adsorbed chemicals by sedimentation in settling basins and lagoons and by filtration in soils are important mechanisms for reducing concentrations in wastewater flows. On the other hand, these deposits represent reservoirs for maintaining concentrations in the transport stream by partitioning or by resuspension of colloidal fractions. Also, their possible impact on desirable biotic communities in lagoons and soils must be considered, as well as their effect on terrestrial systems when sludges are removed for land application.

Distribution coefficients (Kd) have been shown to be related to the degree of inactivation of bioactive compounds in the presence of adsorbing surfaces, as well as to their persistence in soils and sediments. Also, Kd values provide an indication of the extent to which partitioning may serve to maintain the concentration of persistent chemicals residually in waters passing through the system.

Distribution coefficients for raw sewage and treated discharges into storage have been calculated in Table 49 for those chemicals which were present in sufficient concentration to be detected in both solid and liquid phases. The Kd values obtained are in the range of 10^3 to 10^4. These are greater by 2 or more orders of magnitude than have been reported for numerous chemicals in laboratory equilibrations with soils (Hamaker and Thompson, 1972). Values as great as 10^5 have been reported for _p,p_'-DDT, however, in slurry equilibrations with plant tissues, fungal mycelium and muck soils (Shin et al., 1970).

Thus, the distribution coefficients in Table 49 appear valid in the qualitative sense that they illustrate the great capacity of waste solids for concentrating trace organics. They do not provide strong support for more refined interpretation because of the limited number of observations. Certain trends are evident which will warrant detailed investigation in the future.

It is to be expected that different chemicals will be adsorbed to different degrees by any given solid waste component and that adsorption patterns will change as BOD substrates are dissipated. Solids loadings were reduced 50 percent by aeration and settling (from a mean of 253 mg/l to 120 mg/l). The concentration of chemicals associated with residual solids increased (Table 49).

The indicated increase in adsorptive capacity is not unexpected. Adsorptive surface would increase as tissue fragments and aggregated solids are commi-

Table 49. DISTRIBUTION OF TRACE ORGANICS BETWEEN PARTICULATE AND AQUEOUS PHASES, MUSKEGON WASTE WATER, DEC 73 TO DEC 75.

Source		P,P' - DDE	Heptachlor	Heptachlor epoxide	1-hydroxy-chlordane	α-BHC	Lindane	Phorate	Lasso	DEHP
RAW INFLUENT (27 samples total)	No. of samples*	1	2	1	1	1	11	3	2	9
Particulate phase (125 to 576 mg/l) (mean 253 mg/l)	Range: Min	727	146	43	29	113	25	4.x10^{3}	145	30.x10^{3}
	(ng/g) Max		247				2.8x10^{3}	23.x10^{3}	983	3.3x10^{6}
	Mean (ng/g)		196				494	15.9x10^{3}	564	767x10^{3}
Aqueous phase	Range: Min	179	317	6	219	305	15	4.8x10^{3}	20	11.x10^{3}
	(ng/l) Max		437				900	87.x10^{3}	9.3x10^{3}	930.x10^{3}
	Mean (ng/l)		377				233	33.3x10^{3}	4.7x10^{3}	152.x10^{3}
Distribution coefficient†		4.1x10^{3}	.5x10^{3}	7.2x10^{3}	.1x10^{3}	.4x10^{3}	2.1x10^{3}	.5x10^{3}	.1x10^{3}	5.0x10^{3}
DISCHARGE INTO STORAGE (20 samples total)	No. of samples	1	1	1	4	0	9	0	1	8
Particulate phase (49 to 245 mg/l) (mean 120 mg/l)	Range: Min	25.x10^{3}	3.1x10^{3}	50	39	---	250	---	25.x10^{3}	1.3x10^{3}
	(ng/g) Max				1.2x10^{3}		1.4x10^{3}			2.5x10^{6}
	Mean (ng/g)				535		561			1.03x10^{6}
Aqueous phase	Range: Min	17	800	6	5	---	3	---	17	1.0x10^{3}
	(ng/l) Max				137		717			2.0x10^{6}
	Mean (ng/l)				96		158			318.x10^{3}
Distribution coefficient		1.5x10^{6}	3.9x10^{3}	8.3x10^{3}	5.6x10^{3}	---	3.6x10^{3}	---	1.5x10^{6}	3.2x10^{3}

*No. of samples in which chemicals were detected in both particulate and aqueous phases.

† $$\text{Distribution coefficient} = \frac{\text{Particulate phase (ng/g)}}{\text{Aqueous phase (ng/l)}} \times 10^{3} = \text{Kd}$$

nuted by metabolic degradation and physical detrition in aeration lagoons. Also respiratory processes will alter the nature of exposed surfaces, and probable changes would increase specific adsorption of many organic species.

An increase in adsorptive capacity of residual solids would lead to increased distribution coefficients, as evidenced for most chemicals in Table 49. On the other hand, degradation of occluding structures might expose more of a complexed chemical for partitioning and result in a relatively greater increase in concentration in the aqueous phase than in the solid phase, and a decrease in distribution coefficient, as indicated for DEHP.

The distributions in Table 49 are consistent with the evidence in Tables 47 and 48 that incidence and total recoveries of frequently encountered chemicals were not affected (or may have been increased in some cases) by detrital changes during treatment before storage.

Data for 1974 (Tables 47 and 48) suggest that reductions in incidence and concentration of several chemicals may have occurred in consequence of storage. Sedimentation in lagoons would have been a contributing factor. On the other hand, no attenuation during storage was indicated for lindane-related species. This reflects both the recalcitrance of the chlorinated cyclohexanes and their relatively much greater solubility relative to other chlorinated hydrocarbons (Biggar and Riggs, 1974; Gunther et al., 1968).

TRACE ORGANICS IN SOILS

Background Samples

Background data are given in Table 50 for surface soils (0-15 cm) from 25 circles and for subsoils (46-61 cm) from 17 circles sampled at various times in 1972 or 1973. Eight circles were selected to represent four major soil types for routine twice-a-year sampling. These special study stations were sampled for background in spring 1973 and again in spring 1974 just before irrigation with wastewater was initiated. Background data for the six special study sites at Muskegon are given in Tables 51 and 52 and, for the two sites at Whitehall, in Table 56.

Both *p,p*'-DDT and *p,p*'-DDE were encountered in nearly all surface samples, less frequently and at lower concentrations in subsoils. The corresponding *o,p* isomers were encountered less frequently, but at similar concentrations. The anaerobic metabolite, *p,p*'-DDD, was indicated in a few samples, but peaks for *o,p*-DDD were not detected.

Peaks for dieldrin were encountered in about half of the surface soils, less frequently and at lower concentrations in subsoils. Heptachlor was indicated at only one station. This was in circle 44 (MSU site No. 26) in 1973, at which time it was accompanied by the highest value for dieldrin encountered at any time during this study (Table 51).

In later samplings, values for both dieldrin and DDT species have varied widely in circle 44 as compared with other stations (cf. Tables 51 to 55 and next section). The highest values for DDT species in this study were obtained

Table 50. TRACE ORGANICS IN SOILS, MUSKEGON AND WHITEHALL SYSTEMS, BACKGROUND SAMPLES TAKEN SUMMER 72 OR JUNE 73 (25 SURFACE SAMPLES, 17 SUBSOIL SAMPLES).‡

MSU Site No.	Circle No.	Sample depth cm	Dieldrin	*o,p* - DDT	*o,p* - DDE	*p,p'* - DDT	*p,p'* - DDD	*p,p'* - DDE	Heptachlor	Heptachlor epoxide	Total DDT species	Heptachlor plus metabolites
			ng/g									
03	21#	0-15	tr**†	nd	nd	5.0	nd	1.4	nd	nd	6.4	nd
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
04	24#	0-15	nd*	nd	1.4	1.2	nd	.6	nd	nd	3.2	nd
		46-61	nd	nd	nd	nd	nd	.1†	nd	nd	.1†	nd
05	23#	0-15	nd	nd	nd	nd	nd	.7	nd	nd	.7	nd
		46-61	---	---	---	No Analysis		---	---	---	---	---
06	23#	0-15	.3	nd	nd	nd	nd	.4	nd	nd	.4	nd
		46-61	---	---	---	No Analysis		---	---	---	---	---
08	47§	0-15	nd	nd	nd	5.0	nd	1.2	nd	nd	6.2	nd
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11	1#	0-15	nd	nd	nd	nd	nd	.8	nd	nd	.8	nd
		46-61	---	---	---	No Analysis		---	---	---	---	---
14	11#	0-15	nd	nd	nd	.2†	nd	.5	nd	nd	.7	nd
		46-61	---	---	---	No Analysis		---	---	---	---	---
16	41§	0-15	nd	nd	nd	1.3	nd	.8	nd	nd	2.1	nd
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17	42§	0-15	nd	nd	nd	1.1	nd	.5	nd	nd	1.6	nd
		46-61	nd	nd	nd	nd	nd	.1†	nd	nu	.1†	nd

(continued)

#Sites draining to north outfall at Muskegon
§Sites draining to south outfall
†Below usual range of confident quantitation (Aypendix II., Table 2).

Table 50. (continued)

MSU Site No.	Circle No.	Sample depth cm	Dieldrin	o, p - DDT	o, p - DDE	p, p' - DDT	p, p' - DDD	p, p' - DDE	Heptachlor	Heptachlor epoxide	Total DDT species	Heptachlor plus metabolites
			- - - - - -	- - - - - -	- - - - - -	- - - - ng/g	- - - - - -	- - - - - -	- - - - - -	- - - - - -		
18	3#	0-15	tr** †	1.9	nd	1.9	nd	1.3	nd	nd	4.1	nd
		46-61	---	---	---	No Analysis		---	--	--	---	--
19	7#	0-15	.7	nd	nd	1.2	nd	5.6	nd	nd	6.8	nd
		46-61	nd	nd	nd	nd	nd	.2	nd	nd	.2	nd
21	19#	0-15	nd	nd	nd	5.8	nd	3.5	nd	nd	9.4	nd
		46-61	---	---	---	No Analysis		---	--	--	---	--
23	27#	0-15	nd	nd	nd	nd	nd	2.0	nd	nd	2.0	nd
		46-61	nd	nd	nd	nd	nd	.1†	nd	nd	.1	nd
25	40§	0-15	nd	3.1	nd	2.7	.3	2.1	nd	nd	8.2	nd
		46-61	nd	nd	nd	nd	nd	.8	nd	nd	.8	nd
26	44§	0-15	48.0	2.0	nd	5.0	nd	1.4	1.5	tr	8.4	1.5
		46-61	.2	nd	nd	nd	nd	.2	nd	nd	.2	nd
27	40§	0-15	.1†	2.5	nd	.4	nd	1.6	nd	nd	4.5	nd
		46-61	.4	nd	nd	.8	.8	1.0	nd	nd	2.6	nd
29	W-2	0-15	.1†	2.0	nd	2.7	.6	2.2	nd	nd	7.5	nd
		46-61	---	---	---	No Analysis		---	---	---	---	---
30	W-3	0-15	nd	3.4	nd	1.6	1.1	4.1	nd	nd	10.2	nd
		46-61	nd	nd	nd	nd	nd	.2	nd	nd	.2	nd

*nd = not detected

**tr = trace

† Below usual range of confident quantitation (Appendix II, Table 2).

(continued)

Table 50. (continued)

MSU Site No.	Circle No.	Sample depth cm	Dieldrin	o,p - DDT	o,p - DDE	p,p' - DDT	p,p' - DDD	p,p' - DDE	Heptachlor	Heptachlor epoxide	Total DDT species	Heptachlor plus metabolites
31	W-1	0-15	.1†	nd*	nd	2.2	1.0	1.8	nd	nd	5.0	nd
		46-61	nd	nd	nd	.5	nd	.5	nd	nd	1.0	nd
32	W- 2	0-15	nd	nd		1.8	nd	1.1	nd	nd	2.9	nd
		46-61	nd	nd	nd	nd	nd	.1†	nd	nd	.1†	nd
33	33#	0-15	nd	nd		2.3	nd	1.2	nd	nd	3.5	nd
		46-61	nd	nd	nd	.2†	nd	.1†	nd	nd	.3†	nd
34	30#	0-15	nd	nd		4.3	nd	1.3	nd	nd	5.6	nd
		46-61	nd	nd	nd	.2†	nd	.2	nd	nd	.4	nd
35	43§	0-15	nd	nd		2.5	nd	.8	nd	nd	3.3	nd
		46-61	nd	nd	nd	nd	nd	.1†	nd	nd	.1†	nd
36	46§	0-15	nd	nd		1.4	nd	.8	nd	nd	2.2	nd
		46-61	nd	nd	nd	.2†	nd	.1†	nd	nd	.3†	nd
37	42§	0-15	nd	nd		.2†	nd	nd	nd	nd	.2†	nd
		46-61	--	--	----	No Analysis		----	--	--	----	--
Frequency of detection (no. of samples)												
25 samples analyzed: 0-15			8	6	1	21	4	24	1	1	25	1
17 samples analyzed:46-61			2	0	0	5	1	14	0	0	14	0
Range when detected (ng/g)												
		0-15	Min tr	1.9	1.4	.2†	.3	.4	1.5	tr	.2†	1.5
			Max 48.0	3.1	---	5.8	1.1	5.6			10.2	
		46-61	Min .4	---	---	.2†	.8	.1†	---	---	.1†	---
			.4			.8		1.0			2.6	
Mean for samples in which detected (ng/g)												
		0-15	6.2	2.5	1.4	2.4	.8	1.6	1.5	tr	4.2	1.5
		46-61	.3	---	---	.4	.8	.3	---	---	.4	---

‡ GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC Columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 51. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, MUSKEGON, BACKGROUND SAMPLES TAKEN JUNE 73 AND APRIL 74 (SURFACE SOILS, 0-15 cm). ‡

MSU Site No.	Circle No.	Year	Dieldrin	o,p - DDT	o, p - DDE	p, p' - DDT	p, p' - DDD	p, p' - DDE	Heptachlor	Total DDT species
			ng/g							
03#	21	73	tr**†	nd	nd	5.0	nd	1.4	nd	6.4
		74	.1†	.2	nd	1.1	.4	.4	nd	2.1
04#	24	73	nd*	nd	1.4	1.2	nd	.6	nd	3.2
		74	.1†	.2	nd	1.2	nd	.4	nd	1.8
08§	47	73	nd	nd	nd	5.0	nd	1.2	nd	6.2
		74	.4	.6	nd	.9	nd	.4	nd	1.8
26§	44	73	48.0	2.0	nd	5.0	nd	1.4	1.5	8.4
		74	3.1	.5	nd	2.0	.8	1.0	nd	4.4
16§	41	73	nd	nd	nd	1.3	nd	.8	nd	2.1
		74	.8	.4	nd	.9	.6	.5	nd	2.4
17§	42	73	nd	nd	nd	1.1	nd	.5	nd	1.6
		74	.4	.6	nd	1.4	.4	.3	nd	2.8
Frequency of detection (no. of samples) (12 samples analyzed)			8	7	1	12	4	12	1	12
Detected range (ng/g)	Min.		tr	.2	1.4	.9	.4	.3	1.5	1.6
	Max.		48.	2.0		5.0	.8	1.4		8.4
Detected mean (ng/g)			6.6	.6	1.4	2.2	.6	.7	1.5	3.6

*nd = not detected

**tr = trace

#Sites 03 and 04 drain to north outfall (Mosquito Creek).

§Sites 08, 26, 16 and 17 drain to south outfall (Black Creek).

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 52. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, MUSKEGON, BACKGROUND SAMPLES TAKEN JUNE 73 AND APRIL 74 (SUBSOILS, 46-61 cm). ‡

MSU site No.	Circle No.	Year	Dieldrin	o,p - DDT	o,p - DDE	p,p' - DDT	p,p' - DDD	p,p' - DDE	Heptachlor	Total DDT species
						ng/g				
03#	21	73	nd*	nd	nd	nd	nd	nd	nd	nd
		74	nd	nd	nd	nd	nd	nd	nd	nd
04#	24	73	nd	nd	nd	nd	nd	.1†	nd	.1†
		74	.1†	.2	nd	.7	nd	.1†	nd	1.1
08§	47	73	nd	nd	nd	nd	nd	nd	nd	nd
		74	.3	nd	nd	.7	nd	.1†	nd	.8
26§	44	73	.2	nd	nd	nd	nd	.2	nd	.2
		74	.5	nd	nd	.6	nd	nd	nd	.6
16§	41	73	nd	nd	nd	nd	nd	nd	nd	nd
		74	.1†	nd	nd	.5	nd	.2	nd	.7
17§	42	73	nd	nd	nd	nd	nd	.1†	nd	.1†
		74	.1†	nd	nd	.4	.1†	nd	nd	.5
Frequency of detection (no. of samples) (12 samples analyzed)			6	1	0	5	1	6	0	8
Detected range (ng/g)		Min	.1	2	---	.4	.1	.1	---	.1
		Max	.5		---	.7		.2	---	1.1
Detected mean (ng/g)			.2	.2	---	.6	.1	.1	---	.5

*nd = not detected

#=sites 03 and 04 drain to north outfall (Mosquito Creek)

§ = sites 08, 26, 16 and 17 drain to south outfall (Black Creek).

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 53. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, MUSKEGON (NOVEMBER 1974 SAMPLING).‡

MSU site no.	Circle no.	Depth	o,p-DDT	p,p'-DDT	p,p'-DDD	p,p'-DDE	1-hydroxy-chlordene	α-BHC	Lindane	Diazinon	Atrazine	Lasso	DEHP	Total DDT species	Lindane plus isomers
			ng/g												
03#	21	0-15	2.9	2.9	1.4	5.5	nd	1.5	nd	nd	410.	6.0	2.74x10^3	12.7	1.5
		46-61	.1†	nd	nd	2.3	nd	1.0	nd	nd	nd	4.0	2.61x103	2.4	1.0
04#	24	0-15	nd*	nd	nd	nd	.1†	1.9	nd	nd	230.	4.0	2.84x10^3	nd	1.9
		46-61	nd	nd	nd	nd	nd	.1†	nd	4.0†	nd	nd	nd	nd	.1†
08§	47	0-15	nd	nd	nd	nd	nd	1.2	nd	nd	490.	11.0	nd	nd	1.2
		46-61	.5	1.7	nd	1.0	nd	nd	.4	12.0	nd	3.0	nd	3.1	.4
26§	44	0-15	nd	nd	nd	nd	nd	3.0	nd	nd	nd	nd	.33x10^3	nd	3.0
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16§	41	0-15	nd	nd	nd	.9	nd	.1†	1.0	nd	nd	nd	nd	.9	1.2
		46-61	nd	.1†	nd	nd	nd	nd	.1	nd	nd	nd	nd	.1†	.1
17§	42	0-15	nd	nd	nd	nd	nd	.1†	.5	nd	nd	nd	nd	nd	.6
		46-61	nd	nd	nd	nd	nd	nd	.1	9.0	nd	nd	nd	nd	.1
Detected means		0-15	2.9	2.9	1.4	3.2	.1	1.3	.8	---	377.	7.1	1.97x10^3	6.8	1.6
		46-61	.3	.9	---	1.6	---	.6	.2	8.4	---	3.3	2.61x103	1.9	.3

*nd = not detected

sites 03 and 04 drain to north outfall (Mosquito Creek).

§ sites 08, 26, 16, and 17 drain to south outfall (Black Creek).

† Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 54. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, MUSKEGON (APRIL 1975 SAMPLING).‡

MSU site No.	Circle No.	Depth cm	Aldrin	Dieldrin	o,p-DDT	o,p -DDD	p,p'-DDT	p,p'-DDD	p,p'-DDE	α-BHC	Lindane	Methoxy-chlor	Atrazine	Lasso	2,4-D(ME)	2,4-D(IPE)	DEHP	Total DDT species	Lindane plus isomers
			ng/g																
03#	21	0-15	nd*	nd	28.0	nd	3.0	nd	.2	.1†	nd	nd	nd	17	nd	nd	nd	31.2	.1†
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3	nd	nd	nd	nd	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	.4†	nd	3	nd	nd	nd	nd	nd
04#	24	0-15	nd	nd	nd	nd	4.0	nd	1.0	nd	.1	nd	1.4x10^3	39	23.0	tr	6.5x10^3	5.0	.1
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.0	nd	nd	nd	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
08§	47	0-15	nd	nd	1.0	nd	4.0	.6	1.0	nd	nd	nd	12.0†	2†	nd	nd	nd	6.6	nd
		46-61	nd	nd	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.0	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
26§	44	0-15	2.0	29.0	15.0	nd	58.0	14.0	10.0	1.0	nd	nd	nd	nd	nd	nd	nd	97.0	1.0
		46-61	nd	nd	.1†	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	16.0x10^3	.1†	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
16§	41	0-15	nd	nd	nd	nd	1.0	nd	.4	.1†	nd	nd	nd	tr	nd	nd	4.0x10^3	1.4	.1†
		46-61	tr**†	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17§	42	0-15	nd	nd	nd	nd	3.0	nd	.9	1.0	6.0	nd	nd	2†	nd	nd	nd	3.9	7.0
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	.2	nd	nd	2†	nd	nd	nd	nd	.2
		91-107	nd	nd	nd	nd	nd	nd	.1†	nd	.1	nd	nd	nd	nd	nd	nd	nd	.1
Detected means (ng/g)		0-15	2.0	29.0	14.7	--	12.2	7.3	2.2	.6	3.1	--	7.0x10^3	12.1	23.0	.3	5.2x10^3	24.2	1.7
		46-61	tr	--	.1	1.0	---	---	---	--	.1	--	---	2.5	3.0	---	16.0x10^3	.6	.1

*nd = not detected

**tr = trace

#sites 03 and 04 drain to north outfall (Mosquito creek). § Sites 08, 26, 16 and 17 drain to south outfall (Black creek).

†Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 55. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, MUSKEGON (OCT. 1975 SAMPLING).‡

MSU site No.	Circle No.	Depth cm	Dieldrin	o,p - DDT	p,p' - DDT	p,p' - DDE	Heptachlor epoxide	α-BHC	Lindane	Diazinon	Phorate	Atrazine	Lasso	2,4-D (ME)	Total DDT species	Lindane plus isomers
			ng/g													
03#	21	0-15	.4	nd	1.4	nd	nd	nd	4.4	4.6	nd	nd	8	nd	1.4	4.4
		46-61	nd*	nd	nd	nd	nd	nd	.3	nd	nd	nd	nd	nd	nd	.3
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
04#	24	0-15	tr**†	.1†	.8	.2	nd	.4	nd	10.0	nd	108.	4	5.0	1.1	.4
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd	nd	nd
08$	47	0-15	nd	nd	1.9	.8	nd	.6	3.9	3.7†	9.0	31.	1†	nd	2.7	4.5
		46-61	nd	nd	nd	.2	nd	nd	nd	nd	nd	nd	nd	nd	.2	nd
		91-107	nd	nd	.1†	nd	nd	nd	nd	nd	nd	nd	nd	nd	.1†	nd
26$	44	0-15	17.0	nd	1.3	nd	nd	2.0	5.8	nd	nd	36.	58.	1.0	1.3	7.8
		46-61	.2	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd	nd	nd
		91-107	nd	nd	.1†	nd	nd	nd	nd	nd	nd	nd	nd	nd	.1†	nd
16$	41	0-15	nd	nd	2.5	.4	.1	2.5	4.0	6.0	nd	nd	11.	nd	2.9	6.5
		46-61	nd	nd	tr	nd	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
17$	42	0-15	nd	nd	.7	.1	nd	nd	.7	.8†	nd	nd	5.	nd	.8	.7
		46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Detected means (ng/g)		0-15	5.8	.1	1.4	.4	.1	1.4	4.0	5.0	9.0	58.	16.5	3.0	4.7	4.1
		46-61	.2	--	tr	.2	--	---	.3	---	---	---	.1	---	.1	.3

*nd = not detected

**tr = trace

#sites 03 and 04 drain to north outfall (Mosquito Creek). $sites 08, 26, 16 and 17 drain to south outfall (Black Creek).

† Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 56. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, WHITEHALL, BACKGROUND SAMPLES TAKEN JUNE 1973 AND APRIL 1974.‡

MSU site no.	Circle no.	Depth cm	Year	Dieldrin	o,p - DDT	o,p - DDE	p,p' - DDT	p,p' - DDD	p,p' - DDE	Heptachlor	Total DDT species
				-ng/g-							
30	W-3	0-15	73	nd*	3.4	nd	1.6	1.1	4.1	nd	10.2
			74	nd	.2	nd	.9	.1†	.1†	nd	1.3
		46-61	73	nd	nd	nd	nd	nd	.2	nd	.2
			74	nd	nd	nd	nd	nd	nd	nd	nd
31	W-1	0-15	73	.1†	nd	nd	2.2	1.0	1.8	nd	5.0
			74	.1†	nd	nd	1.3	.4	1.2	nd	2.8
		46-61	73	nd	nd	nd	.5	nd	.5	nd	1.0
			74	nd	nd	nd	nd	nd	nd	nd	nd
Frequency of detection (no. of samples) (of 4 samples analyzed)		0-15		2	2	0	4	4	4	0	4
		46-61		0	0	0	1	0	2	0	2
Detected range		0-15	Min	.1	.2	---	.9	.1†	.1†	---	1.3
			Max	.1	3.4	---	2.2	1.1	4.1	---	10.2
		46-61	Min	---	---	---		---	.2	---	.2
			Max	---	---	---	.5	---	.5	---	1.0
Detected means (ng/g)		0-15		.1	1.8	---	1.4	.6	1.8	---	4.8
		46-61		---	---	---	.5	---	.4	---	.6

*nd = not detected

† Below usual range of confident quantitation (Appendix II, Table 2).

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 57. TRACE ORGANICS IN SOILS, SPECIAL STUDY SITES, WHITEHALL (SAMPLINGS OF NOV. 1974, APR. 1975 AND OCT. 1975). ‡

MSU site no.	Circle no.	Sampling date	Depth cm	o,p' - DDE	p,p'-DDT	p,p'-DDE	α-BHC	Lindane	Phorate	Lasso	2,4-D(ME)	DEMP	Total DDT species	Lindane plus isomers
									ng/g					
30	W-3	Nov 74	0-15	nd*	1.5	.8	.6	.2	nd	nd	nd	nd	2.3	.8
			46-61	nd	nd	nd	.3	.2	nd	nd	nd	nd	nd	.5
		Apr 75	0-15	nd	tr**†	nd	nd	nd	nd	nd	nd	nd	tr	nd
			46-61	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
			91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		Oct 75	0-15	nd	2.8	.9	nd	nd	nd	nd	3.6	nd	3.7	nd
			46-61	nd	nd	nd	nd	nd	nd	nd	nd	700.	nd	nd
			91-107	nd	nd	nd	nd	nd	nd	nd	nd	700.	nd	nd
31	W-1	Nov 74	0-15	nd	nd	nd	.3	.1	nd	nd	nd	nd	nd	.4
			46-61	nd	nd	nd	nd	.1	nd	nd	nd	nd	nd	.1
		Apr 75	0-15	nd	.2†	tr	nd	tr	nd	nd	nd	nd	.2†	tr
			46-61	nd	nd	nd	nd	tr	nd	tr	nd	nd	nd	tr
			91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
		Oct 75	0-15	.2	1.5	.1†	nd	tr	64.	nd	13.9	1850.	1.8	tr
			46-61	nd	tr	nd	nd	nd	nd	nd	nd	nd	tr	nd
			91-107	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Detected means (ng/g)			0-15	.2	1.2	.4	.4	.1	64.	---	8.8	1850	1.6	.3
			46-61	---	tr	---	.3	.1	--	.6	---	700	tr	.2

* nd = not detected

** tr = trace

† Below usual range of confident quantitation (Appendix II, Table 2).

‡ GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

for samples taken at this station in April 1975 (Table 54).

The general area of this sampling station was examined just before corn was planted in May 1976. Fragments of boards and timbers were found at one point, together with a number of woven nylon bags of a type used at one time by the basic producer of heptachlor for protective packaging. A service shed was apparently located here and used in connection with farming operations on surrounding areas of predominantly Granby soils. Immediately east of the building site, however, was a sizeable area of shallow muck (5 to 10 ha). Aerial photos taken about 10 years earlier show a north-south field boundary at about the location of the sampling station (near the center of the NW quarter of Sec. 29, R.14W, T.10N; Sheet No. 67, National Cooperative Soil Survey, Muskegon County, 1968).

Thus, the sampling-to-sampling variability in analyses for dieldrin and DDT species in circle 44 can be ascribed to a complex of soils and previous management bordering within the area designated for sampling. The unusual (for this study) values for dieldrin and DDT species can be ascribed to localized concentration of soil residues associated with storage and handling of these chemicals at a field service facility over periods of time in the past.

Maximum values for dieldrin (48 ng/g) and DDT species (97 ng/g) at this station are, in fact, low relative to ranges of concentration reported in national surveys made as recently as 1974 (Roan, 1975). Values reported here for other sampling stations are no more than might be expected in soils after equilibration with global circulation through the atmosphere (Edwards, 1973; Woodwell et al., 1971).

The relative frequencies and concentrations of DDT, dieldrin and heptachlor at this station over the period of this study are consistent with their relative persistence in soils: DDT > dieldrin > heptachlor (Hiltbold, 1974). Other limited local areas of unusual residual concentrations of these persistent insecticides, perhaps others also, undoubtedly exist elsewhere in the Muskegon system at sites associated with earlier farming operations or residences.

Numerous small unreferenced peaks were present in extracts of background soil samples. However, peaks for dieldrin and DDT species were, normally, the dominant peaks differentiated from background.

Post-Irrigation Samples

Referenced Compounds --

Data for three samplings of soils made since wastewater irrigation was initiated at Muskegon (May 1974) are given in Tables 53, 54, 55. At Whitehall, no wastewater was applied until late in the season, shortly before the first post-irrigation samples were taken in Nov. 1974 (Table 57).

With the exception of DDT species, dieldrin and heptachlor or its metabolites, none of the chemicals in Tables 53, 54, 55, and 57 had been detected in background samples taken before the start of irrigation and farming operations in 1974 (cf. Tables 50, 51, 52, and 56.

Frequencies of Occurrence and Ranges of Detected Concentration

The frequency with which trace organics were encountered pre- and post-irrigation in soils at special study sites is summarized in Table 58 (Muskegon) and Table 59 (Whitehall). The ranges of concentration when detected are given in Tables 60 and 61.

With few exceptions, individual chemicals were encountered more frequently in surface soils (0-15 cm) than in subsoils (46-61 cm) and usually at higher concentrations. Samples were taken also at 91-107 cm in spring and fall of 1975, but only p,p'-DDT, lindane, lasso and methoxychlor were encountered, at near limits of quantitation and only once for each chemical (Tables 53, 54, and 55).

Of the chemicals which have been detected in soils only after irrigations began in 1974, all have been detected at some time in incoming wastewater--except methoxychlor and atrazine. Methoxychlor was detected in soil only once and in trace quantities, so its identification is questionable. The presence of atrazine in soils is explained by its use on-site for weed control, both in 1974 and 1975. Lasso was used as an herbicide both years, but also appeared frequently in incoming wastewaters, at concentrations ranging up to 10^4 ng/l (Tables 47 and 48).

Diazinon was used for control of corn rootworm at Muskegon only in 1974. This would have been the likely source for encounters with this chemical at outfalls and in subsoils in the fall of 1974. However, its frequent occurrence in surface soils in the fall of 1975 (Tables 58 and 60) must be ascribed to wastewater inputs in 1975 ranging up to 10^3 ng/l (cf. Tables 47 and 48).

On-site applications of pesticides have not been made at Whitehall. Traces of Lasso detected in subsoils in April 1975 (Tables 59 and 61) may well have entered in wastewater. Wastewater samples for organic analysis were first taken at Whitehall in April 1975, and Lasso was detected in samples taken in May (Table 43).

Lindane and/or its isomers and DEHP have been the most frequently encountered chemicals in incoming wastewaters at Muskegon (Table 47). They were first detected in soils after irrigations began (Table 58). Incoming concentrations of lindane plus isomers have been less at Whitehall (Table 43) than at Muskegon (Table 48), and concentrations in soils have been less (Table 61 vs Table 60). At Whitehall, DEHP was not detected in incoming wastewater until Sep. 1975 (Table 43), and it was first detected in soil in Oct. 1975 (Table 59).

Significant quantities of lindane and α-BHC appear to have been intercepted in surface soils (Tables 53, 54, 55). The indicated concentrations of lindane in surface soils increased from 1974 to 1975. Immobilization in surface layers undoubtedly contributed to the much lower concentrations in

Table 58. FREQUENCIES OF OCCURRENCE, TRACE ORGANICS IN SOILS, MUSKEGON, JUNE 73 TO OCTOBER 75.‡

Chemicals	Surface soils (0-15 cm)					Subsoils (46-61 cm)				
	Jun 73	Apr 74#	Nov 74	Apr 75	Oct 75	Jun 73	Apr 74#	Nov 74	Apr 75	Oct 75
Total samples	6	6	6	6	6	6	6	6	6	6
	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -	-occurrence†-	- - - - -	- - - - -	- - - - -	- - - - -
Aldrin	nd*	nd	nd	1	nd	nd	nd	nd	1	nd
Dieldrin	2	6	nd	1	3	1	5	nd	nd	1
DDT species	6	6	2	6	6	3	5	3	2	2
Lindane & isomers	nd	nd	6	5	6	nd	nd	5	2	1
Heptachlor & metabolites	1	nd	1	nd	1	nd	nd	nd	nd	nd
Methoxychlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Diazinon	nd	nd	nd	nd	5	nd	nd	3	nd	nd
Phorate	nd	nd	nd	nd	1	nd	nd	nd	nd	nd
Atrazine	nd	nd	3	2	3	nd	nd	nd	nd	nd
Lasso	nd	nd	3	5	6	nd	nd	2	2	1
2,4-D species	nd	nd	nd	1	2	nd	nd	nd	1	nd
DEHP	nd	nd	3	2	nd	nd	nd	1	1	nd

† Numbers of samples in which detected.

* nd = none detected.

# First wastewater applications were made in late May 1974, after the Apr. 1974 sampling.

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 59. FREQUENCIES OF OCCURRENCE, TRACE ORGANICS IN SOILS, WHITEHALL, JUNE 73 TO OCTOBER 75.‡

	Surface soils (0-15 cm)					Subsoils (46-61 cm)				
	Jun 73	Apr 74	Nov 74#	Apr 75	Oct 75	Jun 73	Apr 74	Nov 74#	Apr 75	Oct 75
Total samples	2	2	2	2	2	2	2	2	2	2
	occurrences†									
Dieldrin	1	1	nd	nd	nd	nd	nd	nd	nd	nd
DDT species	2	2	1	2	2	2	nd	nd	nd	1
Lindane & isomers	nd*	nd	2	1	1	nd	nd	2	1	nd
Phorate	nd	nd	nd	nd	1	nd	nd	nd	nd	nd
Lasso	nd	nd	nd	nd	nd	nd	nd	nd	1	nd
2,4-D species	nd	nd	nd	nd	2	nd	nd	nd	nd	nd
DEHP	nd	nd	nd	nd	1	nd	nd	nd	nd	1

†Number of samples in which detected.

#First wastewater applications were made in the fall of 1974, before the Nov. 74 sampling.

*nd=none detected

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 60. DETECTED RANGES OF CONCENTRATION. TRACE ORGANICS IN SOILS, MUSKEGON, JUNE 73 TO OCT 75.‡

Chemicals		Surface soils (0-15 cm)					Subsoils (46-61cm)				
		June 73	Apr 74#	Nov 74	Apr 75	Oct 75	June 73	Apr 74#	Nov 74	Apr 75	Oct 75
						ng/g					
Aldrin	min	nd*	nd	nd	2.0	nd	nd	nd	nd	tr	nd
	max										
Dieldrin	min	tr**	.1	nd	29.0	tr	.2	.1	nd	nd	.2
	max	48.0	3.1			17.0		.5			
DDT species	min	1.6	1.8	.9	1.4	.8	.1	.5	.1	.1	tr
	max	8.4	4.4	12.7	97.0	2.9	.2	1.1	3.1	1.0	.2
Lindane plus isomers	min	nd	nd	.6	.1	.4	nd	nd	.1	tr	.3
	max			3.0	7.0	7.8			1.0	.2	
Heptachlor plus metabolites	min	1.5	nd	.1	nd	.1	nd	nd	nd	nd	nd
	max										
Diazinon	min	nd	nd	nd	nd	.8	nd	nd	4.2	nd	nd
	max					10.0			12.0		
Phorate	min	nd	nd	nd	nd	9.0	nd	nd	nd	nd	nd
	max										
Atrazine	min	nd	nd	230.0	12.0	31.0	nd	nd	nd	nd	nd
	max			490.0	1.4×10^3	108.0					
Lasso	min	nd	nd	4.4	tr	1.0	nd	nd	2.7	2.0	
	max			11.4	39.0	58.0			3.9	3.0	tr
2,4-D Species	min	nd	nd	nd	23.3	1.0	nd	nd	nd	3.0	nd
	max					5.0					
DEHP	min	nd	nd	$.33\times10^3$	4.0×10^3	nd	nd	nd	2.6×10^3	16.0×10^3	nd
	max			2.84×10^3	6.5×10^3						

*nd = not detected

**tr = trace

First wastewater applications were made in late May 1974, after the Apr 74 sampling.

‡ GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

Table 61. DETECTED RANGES OF CONCENTRATION, TRACE ORGANICS IN SOILS, WHITEHALL, JUNE 73 TO OCTOBER 75. ‡

Chemicals		Surface soils (0-15 cm)					Subsoils (46-61 cm)				
		Jun 73	Apr 74	Nov 74#	Apr 75	Oct 75	Jun 73	Apr 74	Nov 74#	Apr 75	Nov 75
		-ng/g-									
Dieldrin	min max	.1	.1	nd	nd	nd	nd	nd	nd	nd	nd
DDT species	min max	4.8 10.2	1.3 2.8	2.3	tr .2	1.8 3.7	.2 1.1	nd	nd	nd	tr
Lindane plus isomers	min max	nd*	nd	.4 .8	tr**	tr	nd	nd	.1 .5	tr	nd
Phorate	min max	nd	nd	nd	nd	64.0	nd	nd	nd	nd	nd
Lasso	min max	nd	nd	nd	nd	nd	nd	nd	nd	tr	nd
2,4-D species	min max	nd	nd	nd	nd	3.6 13.9	nd	nd	nd	nd	nd
DEHP	min max	nd	nd	nd	nd	$1.8\text{x}10^3$	nd	nd	nd	nd	700.

* nd = not detected

** tr = trace

#First wastewater applications were made in Fall 1974, before the Nov. 74 sampling.

‡GLC peaks for all chemicals listed in Table 2, Appendix II, were monitored. Only chemicals detected and confirmed on two or more GC columns are reported. Confirmation by thin layer was required, also, except at concentrations too low for spots to be visualized.

subsoils. However, microbial populations with competence to degrade chlorinated cyclohexanes are favored by anaerobic conditions (Kaufman, 1974; Matsumura, 1973). With frequent irrigation, even on these well-drained soils, appropriately oxygen-deficient conditions would likely attain for significant periods at some point in the profile.

Thus, enrichment of subsoils with adaptive microbial populations could have contributed to low recoveries of lindane or other isomers in subsoils and would account for the virtual disappearance of BHC species from drainage at outfalls since early spring of 1975 (Tables 45, 46).

In the case of DEHP, substantial concentrations have continued to appear at outfalls through 1975 (Tables 45 and 46). However, these occurrences have been associated with high hydraulic loadings. The incidence of DEHP in waters passing through the system has declined from sampling point to sampling point (Table 47), and there has been a strong tendency for maximum concentrations to decline also (Table 48). This suggests that populations adapted to degrading DEHP are developing in lagoons and in soils.

Thus, it may be significant that DEHP was not found at any of the 6 special study sites at Muskegon in Oct. 1975 (Table 58). These samples were taken at harvest time and no wastewater had been applied for periods of two weeks or longer on any of the sampled circles. There was very little rain during this period either. The increased retention time afforded by interrupted water applications may have permitted degradation of the latest inputs of DEHP to non-detectable levels.

Lasso has been found in most surface soil samples taken since waste irrigation and agronomic applications were initiated in 1974 (Table 58). Concentrations encountered have increased in surface soils but not in subsoils (Table 60). It appears that this chemical is being intercepted to a large extent in surface soil, but the combined inputs from wastewater and agronomic applications have exceeded the capacity of microbial populations in the surface soil to degrade it.

On the other hand, the incidence of Lasso at outfalls has declined (Tables 45, 46, and 47). Major appearances are associated with planting operations and periods of heavy hydraulic loading. Thus, it may be that mechanisms for removal of Lasso are developing in the soil profile.

Phorate was input frequently with wastewater and in substantial concentrations in 1975 at Muskegon, and 2,4-D species at both Whitehall and Muskegon (Tables 43, 47, and 48). They were encountered in soils for the first time in 1975 (Tables 58 and 59). All except the methyl ester of 2,4-D have appeared at outfalls (Tables 45 and 46).

Phorate is oxidized quickly in soils (Getzin and Shanks, 1970; Hiltbold, 1974; Kaufman, 1974), and 2,4-D esters are quickly hydrolyzed (Loos, 1975). It is to be expected that they might be detected transiently in soils, but for only short periods after input.

Phorate was encountered in soil once in 1975, at Muskegon (Table 55).

The methyl ester of 2,4-D was encountered on three occasions at Muskegon (Tables 54, 55) and twice at Whitehall (Table 57). The other 2,4-D esters were not encountered at credible concentrations in soil, although their presence was indicated in incoming waste water (Tables 39 to 43) and, at Muskegon, in drainage at outfalls (Tables 45, 46).

Soil samples were taken before planting in the spring and during or immediately after corn harvest in the fall. At these times, it was observed that wastewater was being discharged on a number of circles through disconnected sprinkler headers. Areas affected by this off-season dumping of wastewater were avoided in sampling.

The indicated appearance of readily altered compounds, such as phorate and ester derivatives of 2,4-D, in drainage is evidence of excessively rapid transit through the soil. Since soil areas affected by dumping in spring and fall were not sampled, chemicals input at these times would not have been detected in soils even though they did appear in drainage.

"Unknown" Peaks --

Of the three "unknown" peaks monitored in 1975, only one appeared in extracts of soils sampled in October. This peak (R_t = 247-253 sec) was encountered at all three depths in all circles sampled. Peak areas were much less in subsoils than in surface soil. Nevertheless, this was the principal peak in subsoils at Muskegon, accounting for 70 to 99% of total integrated peak area. Proportionate areas for surface soils ranged from 20 to 40% and, for subsoils at Whitehall, from 25 to 55%.

A qualitative assessment, based on these observations, suggests that the chromatographic entity at R_t = 247-253 sec may be a fairly recalcitrant compound. It appears to react rather strongly with surface soil materials but can be displaced downward under conditions of heavy hydraulic loading. It appeared as a prominent peak in 3 of 10 outfall samples taken from August through December 1975 (28 to 37% of total integrated area in the first Florisil eluant). Retention time and behavior on Florisil corresponded to a prominent peak in reference standards for Arochlors 1254 and 1260, but other peaks characteristic for these formulations were not present.

The entity at R_t = 115-118 sec may not interact so strongly with soil materials since the peak did not appear in soil extracts but was prominent in 7 of 10 outfall samples (20 to 40% of total integrated area). It is possible that this is not a single compound, since the peak appeared variably in one or another of the three Florisil fractions.

The third "unknown" (R_t = 164-168 sec) did not show in chromatograms for soil, and the peak encountered in occasional outfall samples was small. The indicated level of input at Muskegon was low. Also more than one species was probably involved, since the distribution among Florisil eluants varied.

EVALUATION OF METHODS

The identification of trace organics in this study was presumptive, based on chromatographic parameters only. Nevertheless, identities were corroborated on three or more media. Circumstantial support for most pesticide species was found in known sales or known patterns of use in river basin areas which drain to Muskegon Lake, Mona Lake or White Lake. Encounters with specific pesticides were associated with weather conditions conducive to runoff and heightened stream flow in these drainage basins.

The observed patterns of encounter with pesticides in wastewaters are significant mainly as evidence that chemicals from non-point sources in extensive regional watersheds can enter these sewage collection systems through connected discharges from industries that draw feedwaters from these lakes or tributary streams. In addition to pesticides and other non-point-source chemicals, the potential exists for entry of chemicals that originate in industrial and municipal discharges at remote outfalls along the tributary streams. For example, twenty industries and nine municipalities use the Muskegon River for wastewater assimilation.

The very much greater and immediate hazard from chemicals input within areas served by the two sewage collection systems was addressed only superficially by methods employed here. In the broad, diverse category of industrial organics, credible data were obtained only for DEHP. At least three other electron-capturing species were present chronically and at indicated concentrations that were frequently greater than for referenced compounds. Numerous small peaks and occasional prominent peaks at retention times not programmed for routine integration were ignored.

The monitored peaks probably account for much of the total mass of electron-capturing species in the GLC column effluent from sample injections. Many chemicals volatile enough to move with the carrier gas stream would not have been detected by electron capture. Derivitization was not employed to permit detection of non-volatiles. Not all polar compounds would have partitioned into the initial methylene chloride extracts, and others would have been eliminated during cleanup and final transfer into hexane.

It has been estimated that no more than 10 or 20 percent of the organics in wastewaters are accounted for by established methods for sampling, extraction, concentration, separation and detection (Donaldson, 1977). The percentage accounted for in the present study was undoubtedly even less.

With regard to sampling, the use of grab samples here was particularly inappropriate for incoming wastewaters because of the episodic nature of inputs, from both industrial and non-point sources. With normal operation, less short-term variation would be expected in irrigation water or drainage because of the large mixing volumes and relatively long retention times in lagoons and soils (Robert S. Kerr Environmental Research Laboratory, 1977). Nevertheless, observed breakthroughs of labile compounds like phorate and 2,4-D esters are evidence that significant short-term discharges to surface streams can occur when unusual operating procedures are employed, as when storage lagoons are by-passed or when wastewater is applied through disconnected sprinkler headers.

Continuous sampling devices would appear essential for incoming waste-waters and at least desirable for other flow points. Analyses should be scheduled more frequently than once a month to increase the likelihood for detection of chemicals input sporadically and to reduce the opportunity for loss or chemical alteration during cumulative storage. To assess performance, for purposes of surveillance and as a guide for on-site management, the frequency of analysis at different flow points should be related to retention times in various components of the system, with due regard for seasonal and ad hoc changes in modes of operation.

Methods used in this study for extraction, concentration, separation and detection were limited in the number of organics which could be detected as well as in the discreteness of separation of such important classes of compounds as chlorinated hydrocarbon pesticides and polychlorinated biphenyls. The range of detectable chemicals can be extended and separations greatly improved by moderately greater detail in preparatory protocol. Substantially greater detail can be achieved, together with increased efficiency, by such measures as the use of selective accumulators in continuous sampling devices to effect preliminary fractionation and concentration, thereby eliminating some of the time consuming steps in the laboratory (Donaldson, 1977).

Electron capture is appropriate for detection of many of the compounds of known concern in industrial discharges into the Muskegon and Whitehall systems. Numerous detection methods are available, covering a wide range of sensitivity and specificity for different types of compounds.

Protocols are being developed for comprehensive analysis of organics in wastewaters, using advanced instrumentation and computer methodologies (Robert S. Kerr Environmental Research Laboratories, 1977). The cost, if large numbers of compounds are to be monitored, will be high. In particular, costs and time constraints will preclude indiscriminate monitoring for the hundreds of compounds of known or suspected hazard.

A feasible protocol for monitoring the Muskegon County systems, or any other, must evolve around a rational ordering of compounds to be monitored. Priorities should be based primarily on known or reasonably suspected consequences of environmental release. National guidelines for establishing priority among potential toxicants are being developed (TSCA Interagency Testing Committee, 1977). However, the determination for a given system should be guided also by the best available information regarding chemicals which are known or reasonably expected to enter the system.

In the case of the Muskegon County systems, several compounds and categories of compounds of recognized hazard have been identified in recent surveys and special studies conducted by state water quality control personnel. These compounds should be given immediate attention in terms of defining input and fate in the treatment systems. Priorities and analytical protocols can be expanded as additional critical compounds are identified in source discharges or as chronic or unusual chromatographic entities at treatment sites. Of crucial importance to this end will be the responsible disclosure of critical materials and campaign schedules by industries within the service areas and in tributary river basins.

Back-up analytical capability for positive identification should be provided, initially at least, by federal or state agencies. Once a chemical has been identified as a chronic input or an expected occasional input from a given source or scheduled process, retention times on appropriate chromatographic media can be used for monitoring. It is possible that recognition by industry of its stake in the integrity of these systems might lead to local funding to support the sophisticated back-up facilities necessary for positive verification or *ab initio* identification of chromatographic entities encountered in source discharges or in combined flows entering the treatment systems.

It is apparent that each compound may interact uniquely with different components of the treatment system. The fate of each should be followed--as a guide both for on-site management and for regulation by public agencies. Data for the referenced chemicals in this study illustrate the influence of operational procedures on renovative effectiveness at the Muskegon site. Observed developmental trends for chronically input species (lindane, heptachlor, related species, DEHP) are encouraging. They suggest that, with appropriate management, land application in combination with economical pretreatment and a period of detention in storage lagoons can very greatly reduce, if not eliminate, the hazards associated with exotic organic toxicants in industrial and municipal wastes.

SUMMARY -- TRACE ORGANICS

1. Local and regional hydrologic systems were described in some detail with a view to identifying probable sources and modes of entry for trace organics into wastewater collection systems at Muskegon and Whitehall.

2. Patterns of encounter with 26 pesticide parameters provide evidence that chemicals from non-point sources can enter these systems through connected discharges from industries that take their feedwaters from Muskegon Lake, Mona Lake, White Lake or tributary streams. By inference, chemicals originating at extramural point-sources can be expected also.

3. A wide range of industrial chemicals which have become the focus of concern in these systems was not addressed by analytical methods used in this study. Credible evidence for chronic entry of DEHP was obtained. Peaks for several unreferenced electron capturing species were present frequently in incoming wastewater but were not identified.

4. In background soil samples, dieldrin and DDT species were indicated at the very low concentrations that might be expected from global circulation, with evidence at one sampling station for locally higher residues from earlier use.

5. Chromatographic peaks observed in incoming wastewaters and peaks for pesticides used on site were found in extracts of soils after the systems were placed in operation in 1974. Both referenced and unreferenced species were found mainly in surface (0-15 cm) and shallow subsurface layers (46-61 cm). Encounters at 91-107 cm were infrequent or at levels approaching the limit for quantitation.

6. Outfalls were monitored only at the Muskegon site. Significant breakthroughs, observed for a number of chemicals, were associated with heavy rains or with seasonally expedient modes of operation that resulted in unusually heavy applications of wastewater on limited soil areas.

7. Data for successive flow points at Muskegon indicate that removals of trace organics occurred both in storage lagoons and during passage through the soil mantle. Chemicals intercepted most effectively were those that are strongly adsorbed by soils or sediments and those that are readily metabolized. Chemicals responsible for unreferenced GLC/ECD peaks appeared to be more recalcitrant or more mobile in soils than the referenced species.

8. Chemicals observed frequently in incoming wastewater (lindane, heptachlor, related species, DEHP) declined in frequency and concentration at outfalls from 1974 to 1975. This is hopeful evidence that the efficiency of the system in removing exotic chemicals may improve over time. Beneficial developmental changes may include the induction of adaptive enzymes in lagoons and soils, increasing volume and adsorptive surface of sediments in lagoons, and increased annual return of crop residues and exudates to support co-metabolism of recalcitrant compounds in soils and residual increases in adsorptive soil organic matter.

RECOMMENDATIONS

Monitoring Priorities

In recent surveys and special studies by control agency personnel, several compounds and categories of recognized hazard have been identified in surface and groundwaters in the Muskegon area. These chemicals should be given immediate but orderly attention in terms of defining input and fate in these treatment systems. An ordering of priorities among candidate compounds is essential for selecting analytical methods that are specific for the compounds sought and realistic in relation to available facilities, personnel and funds.

Relations with Industry

Responsible reporting of critical materials is essential for developing monitoring priorities. In addition to raw materials and major products, listings should include by-products, known or likely, and best determined by the manufacturer. Appropriate confidentiality should be accorded proprietary processes. However, production schedules should be reported in sufficient detail to serve as a guide for monitoring. In particular, monitoring personnel at the treatment sites should be alerted to anticipated critical discharges.

Regulatory pressures and essential adversary positions should be tempered by recognition of the mutual concerns of industry and the general public in maintaining beneficial production consistent with beneficent control of products and by-products. Recent events make it clear that industry's good faith in these matters is essential. In turn, industry should be brought into deliberations leading to choice of regulatory priorities, since cost-benefit distributions are a necessary consideration.

Also, specialized expertise in industry can contribute to development of control technologies. Integration of public and private resources and analytical capabilities can contribute to the effectiveness of monitoring for purposes of surveillance as well as for control of processes both in production and in waste treatment.

On-Site Monitoring

Routine monitoring of waters at key flow points is essential for rational management of the wastewater treatment systems. This can best be done by personnel and analytical facilities at the Muskegon site.

Points to be monitored should permit assessment of changes that occur during important phases of treatment: pretreatment, storage, chlorination, passage through the soil mantle. Continuous sampling at all points is desirable but would appear essential for incoming wastewater and at outfalls. Continuous sampling of incoming wastewater may be more feasible at point of discharge into storage than for raw influent.

Chemicals to be followed within the system should be selected from those for which compliance monitoring is required at outfalls. Internal priorities, must, however, allow for following individual chemicals over sufficient periods of time for their behavior to be reasonably understood and for developmental trends to be expressed. Useful operational data can be obtained most readily for compounds that are input chronically. Flexibility should be developed, also, for following critical chemicals that enter only occasionally.

Frequency of analysis (and frequency of sampling if grab samples are used) should be related to periodicity of inputs and to retention times in different components of the system. It is in this connection that it is important for industries to give accurate and timely notice of production schedules that involve critical discharges into the system.

Requirements for obtaining sound operational data within the treatment systems should be recognized by control agencies in establishing priorities for monitoring in compliance with external regulations. Priorities should be revised as new criteria appear for assessing hazard, or as appropriate analytical capabilities are realized.

RESEARCH NEEDS

Analytical Methods

The development of analytical procedures must proceed hand in hand with the development of monitoring priorities. Both must recognize limitations of available instrumentation, personnel and funds. Methods for a given chemical or group of chemicals should be evaluated and quality control parameters established before routine monitoring is undertaken.

Backup capabilities for positive identification are costly and will need to be supplied, initially at least, by federal or state agencies or through contract with public or private research organizations. Once identities have been established by definitive methods, chromatographic parameters can be used for monitoring and for confirmation with reasonable assurance.

To expedite processing, sampling devices equipped to effect initial fractionation and concentration should be investigated.

Fate of Trace Organics

Useful operational data can be obtained by routine monitoring of waters at key flow points in the system. However, evaluation of management alternatives for prediction purposes over the long term must be based on a fundamental understanding of the extent to which individual chemicals are detained, partitioned, altered or metabolized in different components of the system.

On the basis of data reported here, immediately useful studies might be undertaken with lindane, heptachlor, related species, and DEHP since they appear to be input chronically and because a great deal is known about their interactions (or those of closely related compounds) in natural systems. Of specific concern would be the extent to which induced enzymes, cometabolism or adsorption in soils or sediments may have contributed to increasing effectiveness in removal, as evidenced by decreasing frequencies and concentrations at outfalls.

Chemicals received from industry undoubtedly include numerous photosensitive and photo-sensitizing species. Because of the large area for exposure in storage lagoons, significant photochemical alterations can be expected and should be investigated. Changes due to chlorination after storage should be examined also.

In anticipation of the time when sludges may need to be removed from pretreatment basins or storage lagoons, an inventory should be made of potential toxicants that may have accumulated. Patterns of release during decomposition of sludges in soil should be examined. A continuing concern will be the possibility that specific toxicants may be transferred from sludges or from wastewater into animal feeds and human food channels.

Modeling

Many kinds of information from many sources bear on the successful management and responsible regulation of these systems. To facilitate accumulation, retrieval and manipulation of relevant information, continuing attention should be given to developing comprehensive conceptual models that will include wastewater collection and wastewater treatment in their relation to hydrologic and other systems that can influence or be influenced by them.

Provision should be made to accommodate surveillance fee listings, operational schedules and monitoring data for directly connected point sources as well as for point sources in contributing watersheds. Feedwater sources and volumes for connected industries should be known. Other useful information would include land use parameters, weather data, stream flow data, and sales or management practices that reflect use of critical materials in contributing watersheds.

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APPENDIX 1

METHODS OF ANALYSIS FOR NUTRIENTS

PROCEDURES

Total Carbon

Reagents --

1. Tin Metal Accelerator, Leco Co.
2. Iron Chip Accelerator, Leco Co.
3. Carbon Steel Standards, Leco Co. (0.074 to 0.862% C).

Procedure --

Grind soil samples in a SPEX Industries ball grinder to reduce the particle size. Weigh 50 to 100 mg of soil sample (depending on the carbon content) into ceramic cups.

Add 0.8 g of each accelerator and mix. The sample is placed in the furnace and ignited and total carbon read from the instrument.

Total Nitrogen

Reference --

Bremner, J. M. 1965. Total Nitrogen. Chapter 83 in Methods of Analysis. Agronomy No. 9, part 2. Chemical and Microbiological Properties.

Reagents --

1. Sulfuric acid(H_2SO_4), concentrated.

2. Sodium Hydroxide (NaOH), approximately 10 N: Place 4.2 kg of NaOH in a heavy-walled 10-liter Pyrex flask, add 4 liters of water, and swirl the flask until the alkali is dissolved. Cool and allow to stand for several days to settle out Na_2CO_3, and siphon the clear supernatant liquid into a large Pyrex bottle which contains about 1.5 liters of CO_2-free water and is marked to indicate a volume of 10 liters, and make the solution to 10 liters by addition of CO_2-free water. Mix well and protect from entry of atmospheric CO_2.

3. Boric acid-indicator solution: Place 80 g. of pure boric acid (H_3BO_3) in a 5-liter flask marked to indicate a volume of 4 liters, add about 3,800 ml of water, and heat and swirl the flask until the H_3BO_3 is dissolved. Cool the solution and 100 mls of methyl purple indicator (Fisher's) or add 2 drops of indicator just prior to titration.

4. Potassium sulfate-catalyst mixture: Prepare an intimate mixture of 100 g of K_2SO_4, 10 g of copper sulfate ($CuSO_4 \cdot 5H_2O$), and 1 g of Se. Powder the reagents separately before mixing, and grind the mixture in a mortar to powder the cake which forms during mixing.

5. Sulfuric (or hydrochloric acid)(H_2SO_4 or HCl), 0.01 N standard.

Procedure --

Place a sample containing about 1 mg of N in a dry micro-Kjeldahl flask, add 2 ml of water, and after swirling the flask for a few minutes, allow it to stand for a further 30 minutes. Then add 1.1 g of K_2SO_4-catalyst mixture and 3 ml of concentrated H_2SO_4, and heat the flask cautiously on the digestion stand. When the water has been removed and frothing has ceased, increase the heat until the digest clears, and thereafter boil the mixture gently for 3 hours. Regulate the heating during this boiling so that the H_2SO_4 condenses about one-third of the way up the neck of the digestion flask.

After completion of digestion, allow the flask to cool, and add about 20 ml of water (slowly, and with shaking). Then swirl the flask to bring any insoluble material into suspension. Place 5 mls of boric acid indicator in a 50 ml Erlenmeyer flask and place the flask under the condenser. Connect the micro-Kjeldahl flask to the distillation unit, add 15 mls of NaOH solution (reagent 2) and steam distill until 35 mls of volume is collected. Remove the 50 ml flask, disconnect the steam, and rinse the tip of the condenser into the flask and titrate the ammonium present with 0.01 N acid from a 10 ml graduated burette (graduated in 0.01 ml intervals).

Extractable Ammonium

Reagents --

1. 2N KCl. Weigh 149.2 g KCl into a one liter volumetric flask. Add distilled water to give one liter.

2. 0.1N NaOH. Weigh 4 g of NaOH pellets into a one-liter volumetric flask. Add distilled water to give one liter.

3. Sulfuric (or hydrochloric acid) (H_2SO_4 or HCl), 0.01 N standard.

4. Boric acid-indicator solution: Place 80 g of pure boric acid (H_3BO_3) in a 5-liter flask marked to indicate a volume of 4 liters, add about 3,800 ml of water, and heat and swirl the flask until the H_3BO_3 is dissolved. Cool the solution and add 100 mls of methyl purple indicator (Fisher's) or add 2 drops of indicator just prior to titration.

Procedure --

Weigh 10 gms of moist soil into a 125 ml Erlenmeyer flask, add 50 ml of 2N KCl. Shake for 2 hours on a rotary shaker at 200 rpm. Filter through Whatman #42 filter paper. Pipette 10 mls of filtrate into Kjeldahl flask, attach to steam distillation apparatus, add 10 mls of 0.1N NaOH and steam distil the NH_3 into 5 ml of boric acid-indicator solution. Titrate to endpoint with standard sulfuric acid.

Ammonium Acetate Extractable Cations

Reagents --

1. Ammonium acetate extracting solution: Dilute 114 ml of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 ml of concentrated ammonium hydroxide (NH_4OH), and add water to obtain a volume of about 1,980 ml. Check the pH of the resulting solution, add more NH_4OH as needed to obtain a reaction of pH 7, and dilute the solution to a volume of 2 liters with water.

2. Standard solutions:

Calcium: Dry $CaCO_3$ at 105° c. Then weigh 2.497 g into a 1 liter volumetric flask, add 200 mls distilled water and 75 mls of 2 N HCl. Agitate until dissolved, then dilute to volume with distilled water. Final solution = 1000 ppm Ca.

Magnesium: Clean magnesium ribbon with 0.1 N HCl and wash with distilled water. Dry at 105° c. Weigh 1.0000 g into a 1 liter volumetric flask, add 90 mls 2N HCl and agitate until dissolved. Dilute to volume with distilled water. Final solution = 1000 ppm Mg.

Potassium: Dry KCl at 105° c. Then weigh 1.9066 g into a 1 liter volumetric flask. Add 50 mls 2 N HCl and dilute to volume with distilled water. Final solution = 1000 ppm K.

Sodium: Dry NaCl at 105° c. Then weigh 2.542 g into a 1 liter volumetric flask. Add 50 mls of 2 N HCl and dilute to volume with distilled water. Final solution = 1000 ppm Na.

Procedure --

Weigh 5 g of soil into a 125 ml Erlenmeyer flask and add 50 ml of ammonium acetate extracting solution. Shake for one hour on a rotary shaker at 200 rpm, filter through Whatman No. 2 or equivalent paper, and determine Ca and Mg by comparison with standards on an Atomic Adsorption spectrophotometer and Na and K by comparison with standards on a flamephotometer.

Chelate Extractable Heavy Metals

Reference --

Lindsay, W. L. and W. A. Norvell. 1969. Development of a DTPA Micronutrient Soil Test. Agronomy Abstracts. p. 84.

Reagents -- 1. Extracting solution (0.005 M DTPA, 0.01 N $CaCl_2$ and 0.1 M Triethanolamine): Weigh 3.96 g DTPA 2.22 g $CaCl_2$ and 29.84 g Triethanolamine into a two liter volumetric flask and bring to volume with re-distilled water.

Procedure --

Weigh 10 g soil into 250 ml polypropylene bottles, add 20 ml of extracting solution. Shake on a reciprocal shaker for 2 hours, filter through Whatman number 2 filter paper and analyze the filtrate for Cu, Fe, Mn, Zn, and Pb by comparison with standards on an atomic absorption spectrophotometer.

Digestion with Hydrofluoric and Perchloric Acids for Total Analysis

Reference --

Pratt, P. F. 1965. Chapter 60. In Methods of Soil Analysis Chemical and Microbiological Properties. Agronomy No. 9, Part 2.

Reagents --

1. Hydrofluoric acid (HF), 48%
2. Perchloric acid ($HClO_4$), 70-72%
3. Hydrochloric acid (HCl), 6 N
4. Nitric acid (HNO_3), 70%.

Procedure --

Weigh a 0.5 g sample of finely ground soil in a 30 ml platinum crucible. Wet the soil with a few drops of water, and add 5 ml of HF and 0.5 ml of $HClO_4$. (With surface soils, add 3 ml of HNO_3, heat at 200 C until dry, cool and add 3 ml of HNO_3 and 1 ml $HClO_4$ and heat on a hot plate until the white fumes of $HClO_4$ appear. Cool and add 5 ml HF.) Place the crucible in a sand bath and cover with about nine-tenths of the crucible top with a platinum lid. Heat the crucible to 200 to 225 C and evaporate the contents to dryness. Cool the crucible, and add 2 ml of water and a few drops of $HClO_4$. Replace the crucible in the sand bath, and evaporate the contents to dryness. If organic matter stains are still present on the sides or lid of the crucible, direct the flame of a Meker burner onto the sides and lid until the organic matter is oxidized. Remove the crucible, cool, add 5 ml of 6N HCl and about 5 ml of water. Heat until the solution boils gently. If the sample does not dissolve completely, evaporate the solution to dryness and repeat the procedure, starting with 5 ml of HF and 0.5 ml of $HClO_4$. When the residue completely dissolves in HCl, transfer the sample to a 50-ml volumetric flask, and dilute the content to volume.

Extractable P

Reagents --

1. Extracting solution. Add 15 ml of 1.0 N NH_4F and 25 ml of 0.5 N HCl and 460 ml of distilled water to prepare each 500 mls of extracting solution.

2. Ammonium molybdate-HCl-H_3BO_3 solution. Dissolve 100 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 850 mls distilled water, filter and cool. Add 1700 mls concentrated HCl to 160 mls water, cool. Mix the two solutions slowly and add 100 g of boric acid.

3. Reducing agent mixture. Mix 10 g 1-amino-2-naphthol-4-sulfonic acid with 20 g sodium sulfite and 584 g sodium bisulfite, meta. Grind mixture to a fine powder with morter and pestle.

4. Reducing solution. Dissolve 15.4 g of reagent no. 3 in 100 mls warm distilled water. Cool and filter.

5. Standard phosphate solution: Dilute 0.4393 g of oven-dry KH_2PO_4 to 1 liter in a volumetric flask with distilled water. Working standards are prepared by dilution of this 100 ppm P stock solution.

Procedure --

Weigh 5 g of soil into a 125 ml Erlenmeyer and add 20 mls of extracting solution (reagent no. 1). Shake on a rotary shaker at 200 ppm for one minute, and filter the contents through Whatman No. 2 or 42 filter paper. (1 g of acid washed activated charcoal is added if the filtrates are not clear).

Pipette a 5 ml aliquot of the filtrate into a 50 ml flask. Adjust pH to 3.0 using 2,4 dinitrophenol as an indicator. Add 2 mls of ammonium molybdate solution and about 40 mls distilled water. Shake and add 2 mls of reducing solution, and make to volume with distilled water. Mix and after 10 minutes, but before 15 minutes, measure the color photometrically using 660 mu incident light.

Water Soluble Nitrate

Reagents --

1. Saturated calcium sulfate ($CaSO_4$). Add slightly more than two grams $CaSO_4$ per liter, shake thoroughly and allow to equilibrate overnight before using.

2. Standard nitrate. Weigh 7.216 g of KNO_3 (previously dried for 24 hours at 105 C) into a one liter volumetric flask and add distilled water to give one liter. Working standards of 1 to 50 ppm N are prepared by appropriate dilution of this standard with the calcium sulfate solution.

Procedure --

Weigh 20 grams of freshly sampled soil into a 125 ml Erlenmeyer flask, add 50 mls of saturated calcium sulfate solution. Shake for 1/2 hour on a rotary shaker at 200 rpm. Decant liquid into a 50 ml beaker and measure nitrate content with a specific ion electrode. (Orion electrod for nitrate in conjunction with an Orion 801 meter is presently used in this laboratory.) Standardize the electrode and meter each time with known standards covering the range of nitrate that is in the samples being measured. Also recheck standards after each few analyses.

(Note: For low nitrate contents, the method of Lowe and Hamilton is recommended.)

(Note: Moisture determinations are carried out simultaneously on the soils and the nitrate nitrogen values are reported on a dry wt. basis.)

APPENDIX II.

ANALYTICAL PROCEDURES FOR TRACE ORGANICS IN SOILS AND WATERS

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Methods used in these studies have been drawn from numerous sources. The following (see list of references) have been consulted for guidance in adapting procedures for routine analysis: Pionke and Chesters, 1968; Thompson, 1972; Federal Working Group on Pest Management, 1974, 1975.

The several phases of the operation are considered separately: sampling of soils; sampling of waters; soil extraction; water extraction; separation and clean-up; gas-liquid chromatography; thin layer chromatography; analytical quality control.

SAMPLING OF SOILS

Separate samples are taken at arbitrary increments of depth, depending on the monitoring or other objective. Surface samples through the plow layer may be taken with a core sampler designed to minimize contamination of included increments. Ten cores per sample are composited.

Where subsoils are sampled, a standard 3-inch bucket auger is used. An uncontaminated sample for each desired depth is retained from the central and lower sections of the bucket. A minimum of four auger cores is composited per depth sample.

Composite samples are combined and mixed in the field. The composites are first passed through a stainless steel sieve (5 mm openings) and mixed thoroughly in a 3-gal stainless steel pot. A representative subsample is passed through an 8-mesh stainless steel sieve (about 2mm openings) and again thoroughly mixed before a representative aliquot is taken for the final sample.

Samples are placed in 8 oz brown glass jars with foil-lined screw caps and are stored at 4° C for no longer than one week before extraction.

SAMPLING OF WATERS

For the Muskegon Project, analyses are performed monthly on variously composited water samples. Twice daily grab samples of raw influent and daily grab samples of discharge into storage lagoons and outfalls at Mosquito and Black Creeks have been composited by Muskegon Waste Management System employees and accumulated under refrigeration (4° C) to provide 2 to 3 liters of sample monthly. Collections of pre-chlorination flow and irrigation pump feed water or pan samples from irrigation booms have varied with changes in management routines and availability of personnel.

Water samples are accumulated and stored in brown glass reagent bottles (1 gal cap'y.) with Teflon-lined screw caps.

SOIL EXTRACTION

As soil samples are removed from refrigerated storage, they are stirred and a 10 g sample taken for moisture determination (24 hr at 105° C). Prior to extraction, water is added to a field-moist aliquot (100 g) to adjust to 25% moisture. One hour is allowed for equilibration.

The equilibrated soil sample is extracted with 100 ml of benzene-isopropanol (2:1) in a stainless steel mixing cup. The extraction slurry is mixed for 5 min with a high-speed blender, then allowed to stand overnight. The solvent is carefully decanted into a 500 ml separatory funnel. An additional 100 ml of solvent is added to the mixing cup and the contents blended again for 2 minutes. After standing for 2 hrs, the solvent is transferred to the separatory funnel. A final 50 ml extraction is made by swirling occasionally. This final extract plus benzene-isopropanol rinsings of the cup are added to the separatory funnel.

Five successive 30 ml water washings are used to remove isopropanol. The benzene layer plus benzene washings of the separatory funnel are passed through freshly activated anhydrous sodium sulfate held in a glass funnel into a 100 ml round bottom flask. The benzene is concentrated at 40 - 50° C to less than 10 ml in a rotary evaporator. Then an equal amount of benzene is added, swirled thoroughly, then concentrated almost to dryness. With repeated rinsings of the round bottom flask, the benzene extract is adjusted to 10 ml in a 10 ml vol. flask. The extract is transferred into a glass vial with a Teflon-lined screw cap and is stored at 4° C until cleanup.

WATER EXTRACTION

Water samples may be extracted as received or, if the distribution of chemicals between particulate and aqueous phases is of concern, they may be centrifuged before extraction. Samples of raw sewage and of discharge into storage lagoons at Muskegon were centrifuged routinely through 1975.

Water Extraction for Whole Samples (as received).

The water sample is vigorously shaken by hand and 1.5 liters is immediately extracted in a two liter separatory funnel with 50 ml of methylene chloride.

The solvent layer is then transferred into a 500 ml Erlenmeyer flask. Water is extracted three more times with 50 ml methylene chloride each time. The extract plus rinsings of the funnel are combined in the 500 ml flask. The combined extract is dried by passing through anhydrous sodium sulfate and concentrated by rotary evaporation to 5.0 ml. An equal amount of benzene is added, then concentrated almost to dryness. The residue is quantitatively transferred to a 10 ml volumetric flask, brought up to volume in benzene, and transferred into a glass vial (Teflon-lined cap) for storage at 4° C until separation and cleanup.

Water Extraction for Separating Particulate and Aqueous Phases

A water sample of known volume (1.5 l or more) is distributed in stainless steel bottles and centrifuged in a Sorvall RCB-2 refrigerated centrifuge, equipped with a GSA rotor. Centrifugation at 13,000 rpm (27,300 g) for 20 to 30 min removes most particulate matter from the aqueous phase. Complete separation of particulates can be achieved with excess $CaCl_2$ as flocculating agent.

The supernatant is decanted through a pre-weighed glass fiber filter. A 1.5 l aliquot of the filtered supernatant is extracted immediately in the manner described above for whole samples.

The sedimented solids are transferred quantitatively from the centrifuge bottles to the same glass fiber disc as used to filter the supernatant. The disc is then placed in a solvent-washed glass storage dish and stored at 4°C until it can be prepared for extraction.

When removed from storage, the glass fiber discs and retained solids are dried in a vacuum oven at 50° C (4 hours) and re-weighed. Ten to 20 ml of water is added to the sample in the dish and the cover is taped securely. After 8 hours of standing, 50 ml of benzene-isopropanol (2:1) is added, the cover is securely taped and the contents rotary shaken (100 rpm) for 2 hours. The solvent is decanted into a 250 ml separatory funnel. Two successive 50 ml extractions with 2 hours shaking are then made. After each extraction, the solvent is carefully transferred into the separatory funnel. Three rinsings are made of the filter disc and storage dish.

The benzene-isopropanol extract is washed four times with water to remove the alcohol. The benzene extract is dried by passing through anhydrous sodium sulfate. Dried extract is then concentrated by rotary evaporation and volume adjusted to 10 ml before storing at 4° C until separation and cleanup.

SEPARATION AND CLEANUP

Preparation of Micro Column

Place a small loose plug of Pyrex glass wool in the tip of a 11.2 cm x 1 cm glass column. Pack the column with 2.0 grams of 60/100 mesh Florisil preactivated at 130° C. The column packing is added in increments, each followed by gentle tapping with a vibrator. Place a small loose plug of glass wool again above the surface of the packed absorbent. Store columns in a 130° C oven for at least 48 hours before use.

Florisil Fractionation

(1) Remove Florisil column from the oven and cool to room temperature in a dessicator (1 hr).

(2) Deactivate column with 10 ml of 1% methyl alcohol in benzene mixture.

(3) Elute the column with 10 ml petroleum ether. Discard the eluate. However, take precaution to not allow the column to "run dry" at any time.

(4) Introduce the 10.0 ml of sample extract in benzene slowly into the column, taking care not to disturb the surface of the column absorbent. Begin collection of eluate immediately in a 100 ml round bottom flask. Follow introduction of sample with the first eluant, 50 ml petroleum ether. The fraction eluted by this addition of petroleum ether contains most organochlorine insecticides like lindane, aldrin, heptachlor, o,p-DDE and other compounds like polychlorinated biphenyls.

(5) Elute column with the second eluant: 50 ml of 10% methylene chloride in benzene. Collect eluate in another 100 ml round bottom flask.

(6) Finally collect a third fraction by eluting the column with 50 ml of a mixture of 50 ml benzene, 49 ml methylene chloride and 1 ml acetonitrile. This fraction usually contains most herbicides and phthalates (DEHP). The column can be allowed to drain dry into this final eluant fraction.

Each of the three fractions is concentrated to about 20 ml by rotary evaporation. An equal amount of benzene is added and concentrated to near dryness. The residue is taken up quantitatively in benzene and adjusted to 10 ml. Each fraction is analyzed separately by gas-liquid chromatography and thin-layer. When a chemical is confirmed in more than one eluant fraction, the sum for those fractions is reported.

The use of Florisil as adsorbent and the fractional elution procedure have been adapted from procedures described by Mills (3) and Thompson (5). Various modifications of these procedures, whereby Florisil is partially deactivated with water or other polar solvents (1), have improved the recovery of certain pesticides. The use of a micro-column was proposed by Law and Goerlitz (2). With the micro-column, pesticides are efficiently separated from many interfering coextractives, and the miniaturization contributes to both speed and economy of analysis.

GAS-LIQUID CHROMATOGRAPHY

Identification, confirmation and quantitation of pesticide fractions is performed on a Beckman GC-5 gas chromatograph equipped with a non-radioactive (helium arc discharge) electron capture detector, a 10-in (1 mV) Beckman recorder and an Autolab System I electronic integrator.

Glass columns (3 mm I.D. x 1.83 m) are used, with Gas Chrom Q as solid support. The stationary phase for quantitation is 1.5% OV-17/1.95% QF-1. A second column (6% QF-1) is used routinely for confirmation. Two other columns (2% SE-30 and 3% DEGS) are used occasionally for confirmation of certain chemicals (Table II-2).

Ultrapure helium (Matheson) is used for detector discharge and as carrier gas. The detector is operated at 250° C with a discharge helium flow of 80 ml/min. Column flow rates and temperatures vary with the column (Table II-2).

Instrument parameters are set daily for maximum sensitivity. Normally, amplifier output is attenuated to 2×10^{-9} amps = full scale on the recorder. At this output, maximum CO_2 response at a polarizing voltage of .57 x 150 V is 70 to 80% of full scale. Background current is set with CO_2 slightly in excess of this peak response. Optimum peaks are obtained with a bias voltage of 0.2 to 0.4 x 150 V.

Integrator parameters are set to reject peaks with heights less than 3 times baseline noise; initial peak width is set at 3 to 5 sec, depending on column, and is updated at pre-selected intervals during a run.

Four µl of sample is injected. A multiple standard (in benzene) is injected before each group of three Florisil eluant injections for a given sample. Reference chemicals are selected for each combined standard to assure that the peaks in standard chromatograms are discretely resolved (Table II-2). A separate standard is used for DEHP.

Identification is based on retention time. Quantitation is based on peak area (mV-sec), integrated electronically. During the course of a day's run, the volume of each appropriate standard (Table II-2) is varied from 1 µl to 6 µl (in increments of 2 or 3 µl) to provide coordinates for a standard curve. Response over this range is linear (log-log plot) to about 75% of background current (50 to 60% full scale at attenuated amplifier output = 2×10^{-9} amps). If injected sample quantities do not fall in this range, a new set of standards covering a 1/10 X or 10 X range of concentrations is injected to provide an appropriate standard curve. If extremely high concentrations are encountered, the sample is diluted.

THIN LAYER CHROMATOGRAPHY

Thin layer chromatography is used to substantiate the identity of pesticides detected with two or more GLC columns. The procedure is as follows:

Sample Preparation

Evaporate sample left from G.C. analysis to near dryness (in the vial used for storage) with a flow of high grade nitrogen gas. Add ethyl acetate, shake vigorously and blow down again almost to dryness with N_2. Finally adjust to 0.2 ml with ethyl acetate.

Application of Sample

F-254 silica gel G 250 u plates (Brinkman 66 14180-2) are prescored and activated at 135° C. The pesticide solutions are spotted with disposable capillary tubes at 1 cm intervals along an origin 2 cm from one edge of the plate. Parallel to the origin and 15 cm distant, a second scored line sets the limit for advance of the solvent front. Standard solutions of pesticides to be confirmed are spotted on the same plate as the sample in question.

Development

The developing solvent is a mixture containing 4 ml glacial acetic acid plus 196 ml of a 10% solution of methylene chloride in benzene.

Each plate is developed by ascending chromatography under conditions of equilibrium with free solvent, until the solvent front reaches the second line. Development generally takes 45 min and should be completed within 2 hours of spotting. The plate is then removed from the tank and dried at 60-80° C for 10 minutes.

Detection

The plate is cooled to room temperature, then exposed to short-wave ultra violet light until the spot for the standard of lowest concentration appears, or approximately 10 minutes.

A system similar to one described by Wood (6) is used to make the spots visible for examining later. After developing fluorescence, spray the plate immediately with $AgNO_3$ - bromophenol blue chromogenic reagent. Dry the plate and neutralize excess chromogenic reagent by spraying with iodine solution (1g I_2 + 2 g KI in 300 ml H_2O, diluted 1:1 with acetone just before using).

QUALITY CONTROL

Reagents

Solvents (methylene chloride, benzene, petroleum ether, acetonitrile, methanol) are distilled-in-glass, chromatographic grade (Burdick & Jackson, Muskegon, Mich.). For each new lot a 500 ml aliquot is concentrated to 10 ml and a chromatograph prepared to check for electron-capturing contaminants.

Water for deactivation of soil samples and for use in analytical procedures is double-distilled in glass and adjusted to pH 4.0 before storage in an 18 l Pyrex carboy with a spigot at the bottom equipped with a Teflon stopcock. Each new batch is analyzed as for a water sample to assure absence of electron-capturing species.

Florisil -- 60/100 PR grade (Floridin Co., 3 Penn Center, Pittsburgh, Pa. 15235) -- is transferred immediately upon receipt to glass containers with ground glass stoppers or foil-lined closures and stored in the dark. Each new lot is sampled for extraction with methylene chloride to check for contaminants. Two or three days before use, quantities needed are activated at 130° C for at least 48 hrs, cooled and stored in a desiccator (over P_2O_5). The micro-columns for cleanup are loaded 2 or 3 days before use, stored in an oven at 130° C, then cooled in a desiccator (P_2O_5) just before use. Glass wool plugs are Soxhlet-extracted with methylene chloride for 16 to 20 hrs. Residual methylene chloride is evaporated under an infrared lamp. The plugs are then wrapped in foil and heated at 130° C for 24 hours before they are used in loading the micro-columns.

Glass fiber filter discs (A. H. Thomas 4750 D55) are Soxhlet-extracted with methylene chloride for 24 hours, dried at 130° C, cooled in a desiccator (P_2O_5) and weighed. The weights are scribed on pieces of foil used to separate the discs in a glass storage dish which is kept in the desiccator.

Anhydrous sodium sulfate is Soxhlet-extracted with methylene chloride (50 g/500 ml) for at least 36 hours and dried at 130° C for 48 hours just before use. It should be cooled in a desiccator for an hour before use. For each new lot received from a supplier, the first methylene chloride wash solution is concentrated and taken up in benzene for injection to provide a chromatographic record of possible interfering impurities.

Glassware

Utmost care is taken to avoid contamination of samples or reagents through contact with materials other than glass, stainless steel or aluminum foil. All glass connections (or Teflon-to-glass) are used in tubing for transfer of liquids. Teflon or foil liners are used in all closures.

Rigorous washing procedures are necessary to avoid contamination from glassware:

1. Tap water rinse immediately after use.
2. Hot soak with detergent (Liquinox) and vigorous brushing to remove visible surface deposits.
3. Copious hot water rinse.
4. 12-hour dichromate soak.
5. Copious hot water rinse.
6. Three small rinsings with acetone followed by hexane.
7. Cap with foil until use.
8. Just before use, flush with the solvent to be used at the time.

Reference Standards

Purified reference chemicals are used. Sources are identified in Table 1.

Identification and Confirmation of GLC Peaks

Peaks corresponding to the reference chemicals in Table 2 have been monitored routinely in soils and water from Muskegon and Whitehall. Peaks encountered have been confirmed on two or more GLC columns and by TLC. Three peaks which occur frequently have not been identified (R on 1.5% OV-17/1.95% QF-1 = 115-118 sec, 164-168 sec, 247-253 sec; R_t relative to aldrin = 0.9, 1.27, 1.92).

Peaks for most reference chemicals are resolved satisfactorily on the OV-17/QF-1 column used for quantitation and on the 6% QF-1 column used most frequently for confirmation (Table II-2). For identification of sample peaks, a variation of ± 2 sec is allowed in the retention time for peaks with $R_t <$ 300 sec, increasing to ± 10 for peaks with $R_t >$ 900 sec.

Phorate and α-BHC are separated satisfactorily only on DEGS. On TLC plates, these two chemicals are separated spatially (phorate, $R_f = 0.63$; α-BHC, $R_f = 0.73$), and the spot for phorate is purple, whereas the spot for α-BHC is yellow.

In the case of the sediment phase in untreated sewage influent and of surface soil (0-6 in), there is some ambiguity in resolving peaks for chemicals with retention times on the OV-17/QF-1 column less than 100 seconds (Table II-2). The ambiguities relate primarily to identifying an appropriate baseline on the trailing edge of a broad fused peak for coextracted contaminants. The problem is encountered mainly in the first eluant fraction from Florisil cleanup (Table II-3).

Arochlors that have been examined are eluted almost quantitatively in the first eluant. If present, peaks for PCB components would confound the determination for a number of chemicals in this fraction. Families of peaks typical for commercial Arochlors have not been observed. In particular, frequently prominent unknown peaks at retention times on OV-17/QF-1 of 115 - 118, 164 -168, and 247 - 253 sec were not accompanied by other prominent peaks that would be expected in common Arochlors. Nevertheless, the "windows" specified for selecting referenced peaks for integration would not have excluded a number of PCB species. The possibility that PCB's may have been present at low concentrations cannot be ruled out.

PCB's can be separated from a number of chemicals referenced in this study by available methods (Thompson, 1972). Because of time constraints, these have not been used.

Problems of separation increase with the number of chemicals to be considered in a given survey. Fractional recoveries in Table II-3 provide less than satisfactory separation for the range of chemicals considered in this study. Separations for selected groups of chemicals can be improved by manipulating elutant composition or eluant volumes. Other procedures for fractional separation and concentration are available or are being developed.

The variability in fractional and total recoveries in Table II-3 derives, in part, from the fact that determinations were made by different analysts at widely spaced time intervals during the course of the investigation. Florisil recoveries were not used to adjust values reported in Section VIII of this report.

Extraction Efficiencies

Recoveries of reference chemicals from spiked water samples have ranged from

80 to 110 percent. No attempt has been made to assess efficiency of extraction from spiked soil samples.

Sensitivities and Limits of Quantitation

Instrument parameters are optimized daily for maximum sensitivity. Integrator parameters are set to reject peaks with heights less than 3 times baseline noise. Typically, peak heights representing 50 percent reduction in background current are achieved with injections of 1.3 ng p,p'-DDT or 0.1 ng lindane.

Peak areas for 1 µl standard injections on the quantitating column are given in Table II-2. Quantitation limits in the last column allow for interferences from early-eluting contaminants in sample injections and for decreasing resolution capabilities as peaks widen with increasing elution time. Instrument capabilities vary from time to time. Under optimum operating conditions, smaller peaks can be resolved satisfactorily.

OVERALL ASSESSMENT

Experience in this study serves to emphasize the need to develop and validate analytical protocols for specific chemicals of concern prior to initiation of routine monitoring for those chemicals. Provision must be made for routine assessment of recoveries and possible artifacts at each step. Identification and confirmation by chromatographic procedures should be substantiated by definitive methods as characteristic or unusual wastewater components are encountered. Effective quality control will represent a substantial portion of the total cost for trace organic analysis.

TABLE II-1. REFERENCE CHEMICALS (PURIFIED GRADE) AND SOURCES

Chemical	Chemical name	Source
Aldrin	1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene	Perrine Repository Triangle Park Research Center
Dieldrin	1,2,3,4,10,10-hexachloro-exo-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,exo-5,8-dimethanonaphthalene	Perrine Repository
Heptachlor	1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	Perrine Repository
Heptachlor Epoxide	1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene	Perrine Repository
1-Hydroxychlordene	1,7,8,9,10,10-hexachloro-2,3-6,5 endo-tricyclo [5.2.1.0] deca-4,-8-diene-exo-3-ol	Perrine Repository
Lindane γ-BHC	gamma isomer of hexachlorocyclohexane	Perrine Repository
α-BHC	alpha isomer of hexachlorocyclohexane	Perrine Repository
β-BHC	beta isomer of hexachlorocyclohexane	Perrine Repository
δ-BHC	delta isomer of hexachlorocyclohexane	Perrine Repository
o,p'-DDT	1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane	Perrine Repository
o,p'-DDD	2-(o-chlorophenyl)-2-(p-chlorophenyl-1,1-dichloroethane	Perrine Repository
o,p'-DDE	2-(o-chlorophenyl)-2-(p-chlorophenyl)-1,1-dichloroethylene	Perrine Repository
p,p'-DDT	2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane	City Chem. Corp. New York, N. Y.
p,p'-DDD	2,2-bis(p-chlorophenyl)-1,1-dichloroethane	Perrine Repository
p,p'-DDE	2,2-bis(p-chlorophenyl)-1,1-dichloroethylene	Perrine Repository
Methoxychlor	2,2-bis(p-methoxyphenyl)-1,1,1-trichloroethane	Perrine Repository

(continued)

Table II-1. (continued)

Lasso^{R}	2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide	Weed Science Soc. (City Chem. Corp.)
M. Parathion	O,O-dimethyl-O-(p-nitrophenyl) phosphorothioate	Perrine Repository
E. Parathion	O,O-diethyl-O-(p-nitrophenyl) phosphorothioate	Perrine Repository
Atrazine	2-chloro-4-ethylamino-6-isopropylamino-a-triazine	CIBA-Geigy Chem. Corp.
Diazinon	O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate	Perrine Repository
Endrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo,endo-5,8-dimethanonaphthalene	Applied Sci. Labs (ANSPEC, Ann Arbor, MI)
Phorate	O,O-diethyl-S-(ethylthiomethyl) phosphorodithioate	Perrine Repository
Dimethoate	O,O-dimethyl-S-(N-methylcarbamoylmethyl) phosphorodithioate	Perrine Repository
DEHP	diethylhexylphthalate	Analabs, Inc. New Haven, CT
2,4-D(ME)	methyl ester of 2,4-dichlorophenoxyacetic acid	Perrine Repository
2,4-D(BE)I	n-butyl ester of 2,4-dichlorophenoxyacetic acid	Perrine Repository
2,4-D(BE)II	isobutyl ester of 2,4-dichlorophenoxyacetic acid	Perrine Repository
2,4-D(IPE)	isopropyl ester of 2,4-dichlorophenoxyacetic acid	Perrine Repository
Vegadex^{R}	2-chloroallyl-N,N-diethyldithiocarbamate	Weed Science Soc.

Table II-2. STANDARD SOLUTIONS IN (BENZENE): RETENTION TIMES (R_t) ON FOUR GLC COLUMNS AND TYPICAL SENSITIVITIES AND DETECTION LIMITS FOR THE QUANTITATING COLUMN.

Chemicals	Retention times (R_t) sec column				Quantitating column 1.5% OV-17/1.95% QF-1			
	2% SE-30	6% QF-1	3% DEGS	OV-17/Qf-1	Sensitivities# 1 ul injection	Peak area	Quantitation limits§ Water: ng/l Soil: ng/g	
Column Temperatures (°C)	200	185	185	200				
Column flow rates (ml/min)	50	60	25	60	ng*	mv-sec		
STANDARD A								
α-BHC	49	101	102	70	.010	200	H_2O: Soil:	15. .3
Lindane	59	131	145	90	.005	200	H_2O: Soil:	8. .1
δ-BHC	60	168	103	141	.008	500	H_2O Soil:	8. .1
1-OH-chlordene	108	217	370	167	.016	800	H_2O: Soil:	20. .3
Dieldrin	198	462	273	314	.008	500	H_2O: Soil:	10. .2
pp'-DDD	246	558	683	454	.016	700	H_2O: Soil:	20. .3
pp'-DDT	324	608	683	545	.020	400	H_2O: Soil:	20. .3
Methoxychlor	498	936	---	1055	.104	2,200	H_2O: Soil:	80. 1.
STANDARD B								
Phorate	94	101	63	67	.120	100	H_2O Soil:	300. 5.
Aldrin	108	160	83	130	.005	300	H_2O: Soil:	8. .1
Heptachlor	90	137	90	108	.005	400	H_2O: Soil:	8. .1
Heptachlor Epoxide	132	298	132	204	.004	200	H_2O: Soil:	6. .1
pp'-DDE	198	320	198	292	.012	500	H_2O: Soil:	15. .3
STANDARD C								
2,4-D (ME)	80	108	98	62	.030	200	H_2O: Soil:	50. .8
2,4-D (IPE)	100	132	85	73	.040	200	H_2O: Soil:	100. 2.
2,4-D (BE)I	147	191	109	105	.040	200	H_2O: Soil	100. 2.
2,4-D (BE)II	169	212	128	122	.030	200	H_2O: Soil	60. 1.
Lasso	180	295	146	145	.142	600	H_2O: Soil	150. 3.

(continued)

Table II-2. (continued)

Chemicals	Retention times (R_t) sec				Quantitating column 1.5% OV-17/1.95% QF-1		
	column				Sensitivities# 1 ul injection	Peak area	Quantitation limits§
	2% SE-30	6% QF-1	3%DEGS	OV-17/QF-1	ng*	mv-sec	Water: ng/l Soil: ng/g
	Column Temperatures (°C) 200	185	185	200			
	Column flow rates (ml/min) 50	60	25	60			
STANDARD D							
Diazinon	66	115	62	84	.220	400	H_2O: 350. Soil: 6.
Dimethoate	64	300	442	132	.098	200	H_2O: 150. Soil: 3.
op-DDD	198	382	396	343	.010	400	H_2O: 10. Soil: .2
op-DDT	258	407	385	410	.020	300	H_2O: 20. Soil: .3
Ethyl parathion	125	583	-	240			H_2O: 100. Soil: 2.
STANDARD E							
Atrazine	–	135	193	84	.990	200	H_2O: 1,500. Soil: 25.
β-BHC	180	151	398	105	.020	400	H_2O: 30. Soil: .5
op-DDE	162	295	185	237	.010	400	H_2O: 10. Soil: .2
Methyl parathion	80	442	346	188	0.063	300	H_2O: 100. Soil: 2.
Endrin	222	547	317	385	.010	500	H_2O: 15. Soil: .3
Vegadex	---	---	---	73	.010	200	H_2O: 15. Soil: .3
DEHP	702	1,133	426	980	10.5	1,100	H_2O:10,000. Soil: 170.

* ng/ul = ppm. Primary standards are made up in benzene to contain 10^4 x this concentration. They are stored at 4°C in Teflon-capped vials. Injection standards are prepared at time of use by diluting the primary standard 10^{-3}, 10^{-4} or 10^{-5}. Electron capture detector response is linear on log-log paper for injections of 1 to 6 ul at a given dilution of standard. Sample peaks are quantified by reference to the appropriate linear response curve. Unusually high sample concentrations are diluted.

# Sensitivities at amplifier output attenuated to 2 x 10^{-9} amps = full scale on the recorder.

§ Quantitation limits were estimated from standard curves (6 to 18 runs per chemical), with allowances for baseline noise (3x), for interference from contaminants in sample chromatograms, and for decreasing resolution as peaks widen with increasing retention time. Recoveries from spiked water samples ranged from 80 to 110%. Recovery from spiked soil samples was not determined.

Table II-3. FLORISIL ELUANTS: FRACTIONAL DISTRIBUTIONS AND TOTAL RECOVERIES FOR REFERENCE CHEMICALS.*

Chemical	Distribution % of recovered			Total recovery % of column loading
	Eluant #1	Eluant #2	Eluant #3	
Aldrin	100	---	---	85 - 105
Dieldrin	50 - 90	10 - 50	---	70 - 110
Endrin	60 - 90	10 - 40	---	105 - 145
Heptachlor	100	---	---	85 - 95
Heptachlor epoxide	100	---	---	90 - 110
1-OH-Chlordene	30 - 40	60 - 70	---	90 - 100
Methoxychlor	90 - 95	5 - 10	---	80
o,p-DDT	100	---	---	95 - 115
o,p-DDD	90 - 100	tr - 10	---	70 - 100
o,p-DDE	100	---	---	80 - 115
p,p'-DDT	100	---	---	100 - 120
p,p'-DDD	100	---	---	80 - 100
p,p'-DDE	100	---	---	115
α-BHC	90 - 100	tr - 10	---	80 - 100
β-BHC	100	---	---	80 - 100
γ-BHC (lindane)	100	---	---	70 - 105
δ-BHC	90 - 100	tr - 10	---	75 - 110
2,4-D (ME)	tr - 10	0 - 10	90	50 - 110
2,4-D (BE) I	5 - 20	15 - 25	65 - 70	60 - 150
2,4-D (BE) II	5 - 20	10 - 20	70 - 75	60 - 90
2,4-D (IPE)	10 - 15	10	75 - 80	60 - 65
Diazinon	---	tr - 5	95 - 100	70 - 80
Dimethoate	---	---	100	tr
Parathion (ethyl)	60 - 80	20 - 40	---	90 - 100
Parathion (methyl)	45 - 60	40 - 55	---	80 - 100
Phorate	100	---	---	80 - 100
Atrazine	---	tr - 20	80 - 100	70
Lasso	tr - 5	---	95 - 100	50 - 130
DEHP	---	10 - 25	75 - 90	95 - 100
PCB's:				
Arochlor 1016	100	tr	---	80
" 1221	100	tr	tr	115
" 1242	95	tr	5	100
" 1248	100	tr	tr	90 - 100
" 1254	100	tr	tr	100 - 105
" 1260	100	tr	tr	90 - 120
" 5432	100	---	---	120

* Two determinations for each chemical, using OV-17/QF-1 or SE-30 columns.

APPENDIX III.

The following table has been developed to estimate the nutrients removed by harvested corn grain. They are average values obtained from Ellis et al. 1973.[1]

Table III-1. ESTIMATED NUTRIENT CONTENT OF CORN GRAIN (15.5% MOISTURE).

Nutrient	Content	Quantity Removed by 100 bu/A Corn
		kg/ha
N	1.46%	93
P	0.26%	16.5
K	0.33%	21.0
Ca	0.03%	2.2
Mg	0.12%	7.5
S	0.12%	7.5
Fe	50 ppm	0.3
Mn	10 ppm	0.06
Cu	5 ppm	0.03
An	15 ppm	0.10
Na	0.03%	2.2
Cl	0.03%	2.2

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[1] Ellis, B. G., A. E. Erickson, B. D. Knezek, R. J. Kunze, I. F. Schneider, E. P. Whiteside, A. R. Wolcott and R. L. Cook. 1973. Land Treatment of Wastewater in Southeastern Michigan. Detroit Dist. U.S. Army Corps of Engineers. pp 65 and 68.

APPENDIX IV

AVAILABILITY OF DATA FROM U.S. EPA STORAGE AND RETRIEVAL COMPUTER SYSTEM "STORET"

Much of the data collected has been entered into the U.S. Environmental Protection Agency's storage and retrieval computer system called "STORET". Access to STORET and use of this data may be obtained directly by authorized users or indirectly through any of the ten different EPA Regional Offices or STORET User Assistance, U.S. EPA, 401 M Street, S.W., Washington, D. C. 20460, phone (202) 426-7792. The applicable codes for gaining access to this data are: Agency Code No. 21 MI MUSK; State Code No. 26; County Code No. 121.